SIMULTANEOUS HIGHER ORDER REACTIONS
AND DIFFUSION IN A SLAB

By

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This dissertation is dedicated to my parents and sister without whose support and encouragement it would never have been possible.

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KEY TO SYMBOLS

a   coefficients of the single species second-order kinetic expressions

A   coefficients of the Taylor series expansion of q

Bi   Biot number for mass transfer

c'   normalized dimensionless concentration

c''   normalized dimensionless concentration

$\hat{c}$ dimensional concentration

C   expansion coefficients of the Weierstrass elliptic Pe-function

D   effective diffusivity

g   polynomial invariants for the Weierstrass Pe-function

k   reaction rate constants

L   characteristic length of the slab (i.e. half width)

n   order of a power law rate expression

p   coordinate system identifier for slab, cylinder or sphere

$\wp$ Weierstrass elliptic Pe-function

q   derivative of a concentration with respect to a length scale variable

r   kinetic rate expression

x   dimensional position variable

z   dimensionless position variable, x/L

Greek Letters

α constant in the integration of q, also dummy integration variable

β arbitrary constant in the development of $\hat{c}(0)/\hat{c}_s$

υ stoichiometric coefficient

Φ Thiele, or first-order, or generalized, modulus

η effectiveness factor

Ψ second-order modulus

σ transformation variable during integration

τ transformation variable during integration

X   third-order modulus

Subscripts

A   specific chemical species

B   specific chemical species

C   specific chemical species

eq   equilibrium value

f   forward direction

G   generalized, or normalized, modulus

i   property appropriate to generic chemical species, I

int   internal

j,k   properties appropriate to generic chemical species, J and K

l,m   properties appropriate to generic chemical species, L and M

m+   associated with the surface of repeated equilibrium roots based on the positive square root

m-   associated with the surface of repeated equilibrium roots based on the negative square root

o   at the midplane, $x = 0$ or $z = 0$

P   specific chemical species; or related to product formation in the rate r

Q   specific chemical species

r   reverse direction

R   specific chemical species

s   at the surface of the slab medium, $x = L$ or $z = 1$

1st   first-order

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Analytical solutions are presented for a broad class of simultaneous steady-state, isothermal second-order and third-order reactions and diffusion in a slab-like medium with constant diffusivities. All intrinsically third-order reversible and irreversible kinetic schemes can be unified into a single three-parameter problem, while similar second-order kinetic schemes can be unified into a single two-parameter problem. Analytical solutions for dimensionless concentration profiles, internal effectiveness factors, etc. are determined as functions of these dimensionless parameters: a first-order, or Thiele, modulus, Φ^2_{1st}, a second-order modulus, Ψ, and a third-order modulus, X, for third-order reactions only. The analytical solutions employ the Weierstrass elliptic Pe-function, $\wp$, to characterize the spatial dependence of the concentration profile. The analysis provides semi-quantitative conditions for both diffusion free and diffusion limited behavior. The

modulus, Ψ, is especially adjustable by varying physical parameters. Other limiting interrelationships between the three moduli are developed that restrict the size of the feasible solution space for conventional second-order and third-order reactions. Existing approximation methods are only partially validated. Errors exceeding 20% are quite possible. Improvements to some methods are suggested by the analysis. Autocatalytic second-order and third-order reactions do not conform to established norms for conventional reversible and irreversible reactions. Internal effectiveness factors well in excess of unity are observed. The analytical solution methods developed here are valid for either the Dirichlet or Robin's boundary condition at the surface. These methods apply to varying degrees for selected multiple reaction systems, such as parallel reactions of different orders and Van der Vusse kinetics. As an overall consequence of these developments, the number of elementary chemical reactions possessing an analytical solution for simultaneous reaction and diffusion has increased tremendously.

CHAPTER 1
AN INTRODUCTION TO THE PROBLEMS OF SIMULTANEOUS REACTION AND DIFFUSION IN A SLAB WITH A REVIEW OF PREVIOUS RESULTS

Introduction

The study of the theory of isothermal, coupled, steady-state reaction and diffusion problems dates back to the time of E. W. Thiele and his seminal paper: "Relation Between Catalytic Activity and Size of Particle". The concepts of a modulus, characteristic of the reacting species, and of a ratio of actual achieved rate to maximum possible external rate of a chemical reaction were presented there. Such moduli bear Thiele's name today, while the reaction rate ratios are referred to as internal effectiveness factors. Thiele derived solutions for the case of a first-order irreversible single species reaction with constant diffusivity and a Dirichlet surface boundary condition for both a sphere and an infinite slab of finite thickness. Also derived was an expression for the internal effectiveness factor of a single species irreversible second-order reaction in a slab. More will be said about this result later.

The fifty years following Thiele's work saw the addition of analytical solutions for single reactions with zeroth-order kinetics, with Robin's boundary conditions, in cylindrical coordinates, and a thorough analysis of the first-order problem with multiple reactions, as well as geometries with two or three characteristic length scales such as the

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rectangular parallelepiped. It was recognized by Aris (1957, 1975) that use of the proper characteristic length scale brought the results for different geometries into asymptotic agreement. It was further recognized simultaneously by Bischoff (1965), Aris (1965), and Petersen (1965) that the use of a specially normalized, or generalized, Thiele modulus brought the internal effectiveness factor results for arbitrary kinetics into asymptotic agreement at both large and small modulus magnitudes. This work was collected and summarized by Rutherford Aris in 1975. Some of the emphasis in this field shifted from analytical to numerical solutions with the proliferation of high speed computers in the 1960's. The first studies on the behavior of Langmuir-Hinshelwood kinetics coupled with diffusion began to appear; see Aris (1975) or Satterfield (1970) for summaries. Problems with complex pore networks, nonisothermal reactions, variable diffusivities, reactions with volume changes, etc. were analyzed by numerical methods.

However, after all of this effort, published analytical solutions for the concentration profiles of single reaction systems, either reversible or irreversible, existed only for the following rate laws:

(1)　　$r_f = k_1, \; \hat{c}_1 > 0$　　　$r_f = 0, \; \hat{c}_1 = 0$

(2)　　$r_f = k_1 \hat{c}_1$

(3)　　$r_f = k_1 \hat{c}_1 - k_2$　　　　restrictions on k_2 may apply

(4)　　$r_f = k_1 \hat{c}_1 - k_2 \hat{c}_2$

(5)　　$r_f = k_1 \hat{c}_1^2$

where the result published for (5) was only for the concentration at the slab midplane. This work derives analytical solutions for 25 elementary kinetic rate laws for irreversible

and reversible third-order and second-order reaction systems. It also explains how to derive analytical solutions for five second-order and third-order reactions reversible with a zeroth-order reaction. Additional solutions for several simple parallel reactions with second-order and/or third-order terms are also derived, as well as solutions for about 17 types of autocatalytic behavior undergoing net second-order or third-order kinetics. These analytical solutions are restricted to assumptions of constant diffusivity, infinite slabs, and isothermal behavior; however, both the Dirichlet and Robin's problems are successfully analyzed.

Past studies of problems of simultaneous reaction and diffusion are now a part of traditional chemical engineering. Advances in this area tend to inherit some of this established relevance. What other reasons are there to study such problems? First and foremost, simultaneous reaction and diffusion problems have considerable industrial significance due to the importance of supported catalysts in many commercial processes. Secondly, while this problem was first identified over 50 years ago, there are only a handful of single reaction kinetics which have an analytical solution in some geometry. Methods were developed for approximating behavior in arbitrary catalyst geometries once a solution was found in one geometry. This was an inducement to create a library of analytical solutions in some geometry that has never been fully exploited. Thirdly, certain types of theoretical analyses require an analytical solution as a starting point. For example, when the reaction occurring is exothermic, there is a potential for the reaction and diffusion problem to possess multiple steady states. One type of analysis which assumes an isothermal pellet with a temperature gradient confined to an external

boundary layer is often valid. The analysis of the multiplicity of steady states as a function of the problem data has been done for such first-order reaction problems, Burghardt and Berezowski (1990). It is now possible to extend these analyses to second-order and third-order problems. Finally, the behavior of many problems can be approximately preserved through linearizations of the variables. The analysis of the linearized problem is generally easier to perform. Nonlinear behavior is, nevertheless, best studied directly. Elementary reactions involving autocatalysis are an excellent example. They will be seen to exhibit behavior well outside the range found in linear problems of simultaneous reaction and diffusion.

General Problem Statement

The governing equation for one-dimensional, isothermal, steady-state, simultaneous reaction and diffusion in an infinite slab of finite thickness for the concentration of species, i, $\hat{c}_i$, takes the form

$$D_i \frac{d^2 \hat{c}_i}{dx^2} = v_i r_P \qquad 1.1$$

where r_P is the rate of product formation, D_i is the effective diffusivity of species i, x is the length scale variable measured from the slab midplane to the surface, and v_i is the stoichiometric coefficient of i in the reaction described by r_P. Two geometries for the problem in a slab are illustrated in Figure 1.1, parts a and b. Identical external conditions are assumed when there are two exposed surfaces in order to give a symmetric
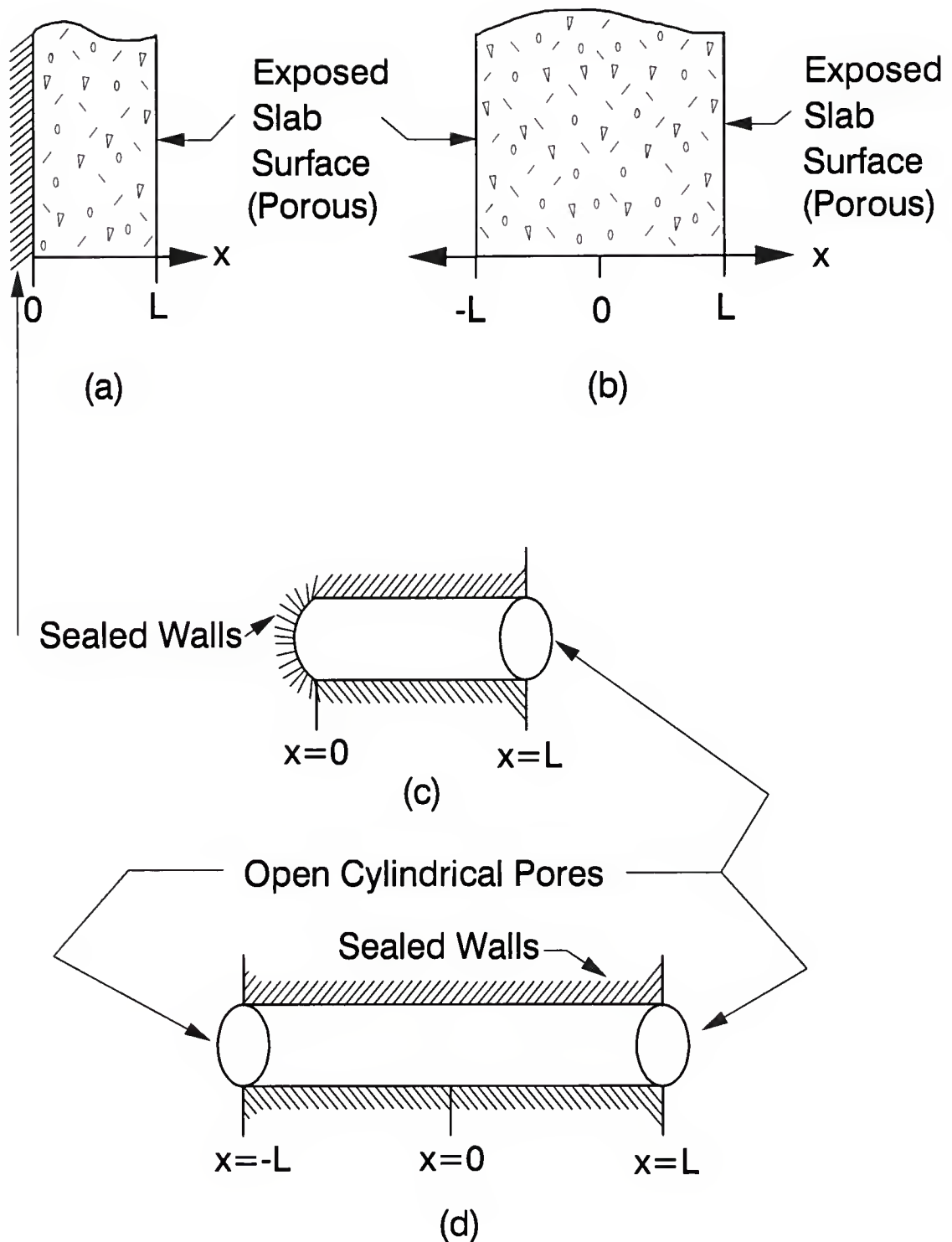
Figure 1.1 The Geometries for the Simultaneous Reaction and Diffusion Problem. (a) the sealed slab, (b) the symmetric slab, (c) the sealed cylindrical pore, and (d) the symmetric cylindrical pore.

problem about the slab midplane. The slab medium is infinite in the y and z directions. Two additional geometries, or interpretations, are shown in Figure 1.1, parts c and d. The cylindrical pore interpretation requires an assumption to neglect radial concentration gradients, which, for surface driven heterogeneous reactions amounts to making the kinetics homogeneous within the pore as well. The analysis to follow for second-order and third-order kinetics requires identical conditions at $\pm L$, where L is the slab half-width. The imposition of net gradients across the 2L wide systems gives a slightly altered final equation to integrate, but analytical solutions may still be possible; see Ince (1927). The boundary conditions for the Dirichlet problem are

$$\hat{c}_i = \hat{c}_{is} \quad at \quad x = L \qquad\qquad 1.2$$

$$\frac{d\hat{c}_i}{dx} = 0 \quad at \quad x = 0 . \qquad\qquad 1.3$$

The boundary conditions for the Robin's problem are

$$k_{gi}(\hat{c}_{if} - \hat{c}_{is}) = D_i\left(\frac{d\hat{c}_i}{dx}\right)_L \quad at \quad x = L \qquad\qquad 1.4$$

$$\frac{d\hat{c}_i}{dx} = 0 \quad at \quad x = 0 \qquad\qquad 1.5$$

where $\hat{c}_{if}$ is the concentration of i in the free stream fluid away from the surface, and k_{gi} is the mass transfer coefficient for species i from the free stream fluid to the slab surface. The following additional result is very important for systems where r_P depends on the concentration of more than one species

$$\frac{D_i}{v_i}\frac{d^2\hat{c}_i}{dx^2} = \frac{D_j}{v_j}\frac{d^2\hat{c}_j}{dx^2} = r_P \ .$$ 1.6

Integration of eq. (1.6) from x = 0 to x gives

$$\frac{D_i}{v_i}\frac{d\hat{c}_i}{dx} = \frac{D_j}{v_j}\frac{d\hat{c}_j}{dx}$$ 1.7

using the boundary condition at x = 0 common to the Dirichlet and Robin's problems. Integration of eq. (1.7) from x to x = L gives

$$\frac{D_i}{v_i}(\hat{c}_i - \hat{c}_{is}) = \frac{D_j}{v_j}(\hat{c}_j - \hat{c}_{js})$$ 1.8

for the Dirichlet or Robin's problem. Eq. (1.8) can be used to eliminate the $\hat{c}_j$ in r_P in favor of a single $\hat{c}_i$. Eqs. (1.8) and (1.4) can be combined to eliminate all but one of the unknown surface concentrations in the Robin's problem boundary condition; however, this is not necessarily desirable. (As an alternative the surface concentrations could be carried along as implicit parameters or replaced with the internal effectiveness factor.) This point will be examined further later in this chapter as well as in Chapter Four. Relationships such as eq. (1.8) permit expressing the $\hat{c}_j$ in terms of one $\hat{c}_i$, either explicitly for the Dirichlet problem, or implicitly through the unknown $\hat{c}_{js}$'s for the Robin's problem. The single species reaction rate expression that results is valid within

the slab only, since that is the range of eq. (1.8). The resulting rate expression does not give the bulk fluid reaction rate correctly except for special cases.

The Zeroth-Order Reaction

A zeroth-order reaction is one that is independent of concentration so long as reactant remains present. This gives a two part governing equation

$$D\frac{d^2\hat{c}}{dx^2} = \begin{pmatrix} k & \hat{c} > 0 \\ 0 & \hat{c} = 0 \end{pmatrix}. \qquad 1.9$$

The solution for the Dirichlet problem is

$$\frac{\hat{c}_s - \hat{c}}{\hat{c}_s} = \left(\frac{kL^2}{2D\hat{c}_s}\right)\left[1 - \left(\frac{x}{L}\right)^2\right] \qquad \frac{kL^2}{2D\hat{c}_s} \le 1 \qquad 1.10$$

or, for $kL^2/2D\hat{c}_s > 1$, is

$$\frac{\hat{c}_s - \hat{c}}{\hat{c}_s} = \left(\frac{kL^2}{2D\hat{c}_s}\right)\left[1 - \left(\frac{x}{L}\right)^2\right] - 2\left(\frac{x^*}{L}\right)\left(\frac{kL^2}{2D\hat{c}_s}\right)\left[1 - \left(\frac{x}{L}\right)\right] \qquad x^* \le x \le L \qquad 1.11$$

$$\frac{\hat{c}_s - \hat{c}}{\hat{c}_s} = 0 \qquad 0 \le x \le x^* \qquad 1.12$$

$$x^* = L\left(1 - \sqrt{\frac{2D\hat{c}_s}{kL^2}}\right). \qquad 1.13$$

Solutions of this type are somewhat awkward because of the transition point, x^*, at which both $\hat{c}$ and $d\hat{c}/dx$ are zero, superseding the usual boundary condition at $x = 0$. These solutions do suggest likely forms for a dimensionless concentration and length, as well

as one additional dimensionless group, $kL^2/2D\hat{c}_s$, which is the square of the Thiele modulus for a zeroth-order reaction, Φ_k. The above solutions could be written

$$c = \Phi_k^2(1 - z^2) \qquad \Phi_k \leq 1 \qquad\qquad 1.14$$

where

$$\Phi_k^2 = \frac{kL^2}{2D\hat{c}_s}, \quad z = \frac{x}{L}, \quad c = \frac{\hat{c}_s - \hat{c}}{\hat{c}_s} \qquad\qquad 1.15$$

or, for $\Phi_k > 1$,

$$c = \Phi_k^2(1 - z^2) - 2(\Phi_k^2 - \Phi_k)(1 - z) \qquad z^* \leq z \leq 1 \qquad 1.16$$

$$c = 0 \qquad 0 \leq z \leq z^* \qquad\qquad 1.17$$

$$z^* = \left(1 - \frac{1}{\Phi_k}\right). \qquad\qquad 1.18$$

It should be noted that the Thiele modulus contains the surface concentration. This is typical of all but first-order reaction systems, and complicates the transition from the Dirichlet to the Robin's boundary condition problem. The solution to that zeroth-order problem will not be needed in what follows, but zeroth-order Dirichlet problem results will occasionally be drawn on for comparison purposes. This review also serves to remind the reader of the possible complications that a zeroth-order reaction could bring to a reversible reaction problem where the opposing reaction is not zeroth-order. Generally, a real species should be associated with the zeroth-order reaction, and safeguards should be taken to see that the concentration of this species is never less than zero.

The First-Order Problem

First-order kinetics must be discussed in this work, since second-order and third-order kinetics were found to behave identically to first-order kinetics for some special cases or under asymptotic conditions. Somewhat more involved expressions for the dimensionless concentration will be developed for second-order and third-order kinetics than are normally used for the first-order problem. The first-order kinetics problem review will be made using a new dimensionless concentration that was found to be the most generally useful

$$c''(z) = \frac{D_i(\hat{c}_{is} - \hat{c}_i(x))}{v_i L^2 r_{Ps}}$$

1.19

where r_{Ps} is the rate of product formation evaluated at the surface of the slab, and z is x/L. Note that if the reaction is in a state of equilibrium at the surface, this equation would call for division by zero. This dimensionless concentration in eq. (1.19) is a universal, or species independent, dimensionless concentration, since

$$\frac{D_i(\hat{c}_{is} - \hat{c}_i)}{v_i} = \frac{D_j(\hat{c}_{js} - \hat{c}_j)}{v_j}$$

1.20

for the symmetric Dirichlet and Robin's problems discussed here. Using this dimensionless concentration here will familiarize the reader with some of its attributes.

Throughout this work, reactant species will be taken as A, B,... and product species will be taken as P, R,... The "forward" reaction rate constant, k_f, will be associated with reactants, and the "reverse" reaction rate constant, k_r, will be associated with products. Whether the forward reaction rate is actually larger than the reverse reaction rate will be irrelevant. Consider the reversible first-order reaction A $\rightleftarrows$ P. The governing equations are

$$D_A \frac{d^2 \hat{c}_A}{dx^2} = -k_r \hat{c}_P + k_f \hat{c}_A \qquad 1.21$$

$$D_P \frac{d^2 \hat{c}_P}{dx^2} = k_r \hat{c}_P - k_f \hat{c}_A . \qquad 1.22$$

Taking $z = x/L$ along with eqs. (1.19) and (1.20) converts both eqs. (1.21) and (1.22) into

$$\frac{d^2 c''}{dx^2} = \left(\frac{k_f L^2}{D_A} + \frac{k_r L^2}{D_P} \right) c'' - 1 . \qquad 1.23$$

Setting either k_r or k_f to zero recovers the irreversible reaction problem for A or P respectively. The minus one term in eq. (1.23) does not vanish for irreversible reactions. The definition of c'' in eq. (1.23), however, alters through r_{Ps} changing when the problem is made irreversible. The formulation in eq. (1.23) retains the boundary condition at x = 0 as

$$\frac{dc''}{dz} = 0 \qquad z = 0 \qquad\qquad 1.24$$

and has the second boundary condition

$$c'' = 0 \qquad z = 1 \qquad\qquad 1.25$$

because of the definition of c'' in terms of $(\hat{c}_{is} - \hat{c}_i)$. Achieving a zero valued surface concentration will give essential flexibility when trying to limit the parameter space dimension for second-order and third-order reaction systems. Rewrite eq. (1.23) as

$$\frac{d^2 c''}{dx^2} = \Phi_{1st}^2 c'' - 1 . \qquad\qquad 1.26$$

The square of the first-order, or Thiele, modulus, Φ_{1st}, is recognized as the sum of the squares of the two Thiele moduli for the irreversible forward reaction, A →, and the irreversible reverse reaction, P →, given by

$$\Phi_A = L\sqrt{\frac{k_f}{D_A}} \qquad\qquad \Phi_P = L\sqrt{\frac{k_r}{D_P}} . \qquad\qquad 1.27$$

The stoichiometric coefficients were assumed to be ± 1, but this restriction can be lifted in which case

$$\Phi_{1st}^2 = v_P \, \Phi_P^2 - v_A \, \Phi_A^2 \, .$$ 1.28

Expressions that possess the feature of a stoichiometric coefficient weighted sum over all species, such as this one for the coefficient of c'', will be found to persist for second-order and third-order reaction systems. The solution of eq. (1.26) is straight forward by conventional techniques for linear second-order differential equations with constant coefficients and gives

$$c''(z) = \frac{\cosh(\Phi_{1st}) - \cosh(\Phi_{1st} z)}{\Phi_{1st}^2 \cosh(\Phi_{1st})}$$ 1.29

There is a less conventional technique for solving eq. (1.26), that begins by multiplying by dc''/dz and integrating from z = 0 to z that yields

$$\frac{1}{2}\left(\frac{dc''}{dz}\right)^2 = \frac{\Phi_{1st}^2}{2}(c''^2 - c''(0)^2) - (c'' - c''(0))$$ 1.30

where c''(0) is an as yet unknown value of the solution. From eq. (1.30) one can derive the following

$$\left(\frac{dc''}{dz}\right)_{z=1} = \pm\sqrt{2c''(0) - \Phi_{1st}^2 c''(0)^2} \, .$$ 1.31

The dimensionless surface concentration gradient depends only on the Thiele modulus and dimensionless midplane concentration. Formulae of this type will recur in Chapters Two and Three for second-order and third-order kinetics respectively. The integration of eq. (1.30) can be continued by conventional methods after separation of variables, ultimately leading to the expression for c''(z) obtained above.

Since c'' was taken as zero at the surface, it might be thought that c''(0) is unconstrained in magnitude. This is not the case, however, for first-order reversible and irreversible reactions as shown in Figure 1.2. The expression for c''(z=0) can be written as

$$c''(0) = \frac{1 - 1/\cosh(\Phi_{1st})}{\Phi_{1st}^2} \qquad 1.32$$

with the two limiting values

$$\lim_{\Phi_{1st} \to 0} c''(0) = \frac{1}{2} \qquad \lim_{\Phi_{1st} \to \infty} c''(0) = \frac{1}{\Phi_{1st}^2}. \qquad 1.33$$

The limit at infinity is a zero of the right-hand side of eq. (1.26). It corresponds to $k_f \hat{c}_A(0) - k_r \hat{c}_P(0) = 0$, as can be shown by substituting into eq. (1.19). The right-hand side of eq. (1.26) is a diffusion modified reaction rate expression, and a zero of this is a statement of positional equilibrium in the slab medium. The limit as Φ_{1st} goes to zero has physical significance as well. In eq. (1.26) take $\Phi_{1st}^2 c'' - 1 = -1$, the dimensionless
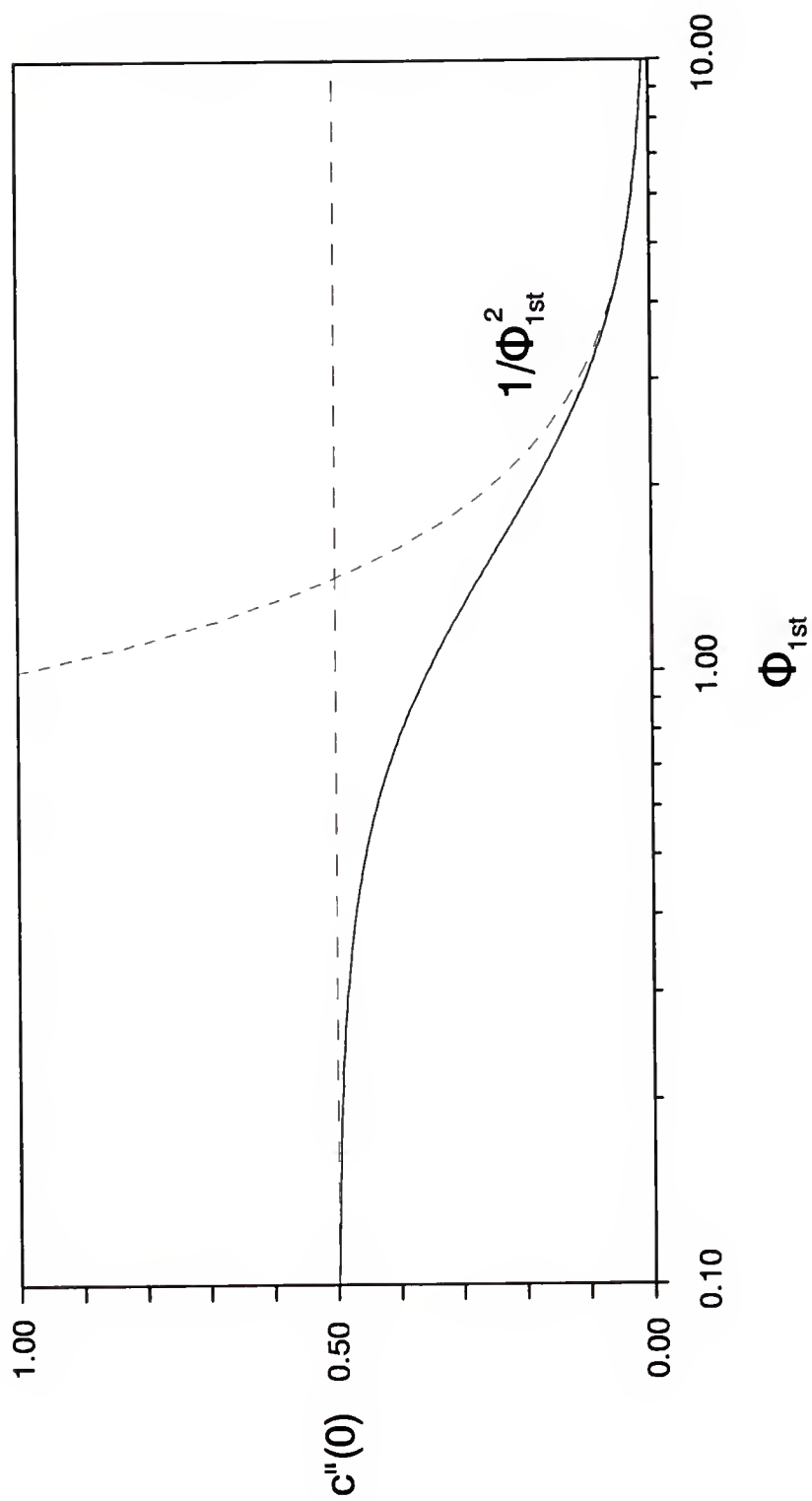
Figure 1.2 The Dimensionless Midplane Concentration for First-order Reactions.

surface reaction rate. Integrate twice to obtain

$$c''(z) = -\frac{z^2}{2} + az + b.$$
1.34

Applying the Dirichlet boundary conditions gives

$$c''(z) = \frac{1}{2}(1 - z^2) \qquad c''(0) = \frac{1}{2}.$$
1.35

Thus $c''(0) = 1/2$ symbolizes a uniform reaction rate from the slab surface to the midplane. Figure 2 further suggests that $0.2 < \Phi_{1st} < 5$ contains the majority of the transition from one limit to the other.

The Robin's boundary condition transforms to

$$Bi_{mi}c''_{fi} = \frac{dc''}{dz} \qquad z = 1$$
1.36

where $Bi_{mi} = k_{gi}L/D_i$ is the Biot number for mass transfer for species i. Equivalently by eq. (1.31),

$$Bi_{mi}c''_{fi} = -\sqrt{2c''(0) - \Phi_{1st}^2 c''(0)^2}.$$
1.37

Reasons for choosing the minus sign are essentially physical. The dimensionless surface concentration, zero, is expected to lie between the dimensionless midplane concentration,

positive, and the dimensionless free stream concentration. Therefore the dimensionless free stream concentration is expected to be negative. A further reason for choosing the minus sign in eq. (1.31) will be given below. Insertion of the c''_f expression into eq. (1.19) gives $\hat{c}_{is}$ for known $\hat{c}_{if}$. Knowledge of $\hat{c}_{is}$ plus $c''(z)$ gives $\hat{c}_i(x)$. Since Φ^2_{1st} is independent of $\hat{c}_{is}$, $\hat{c}_{js}$, etc. for first-order reactions, the final solution for the Robin's problem is immediately obtained from the Dirichlet problem in its present form. Some of the useful features of the c'' formulation are that its midplane concentration is bounded even though its surface concentration is zero, that the choice of roots in equations like eq. (1.31) are easily made, and that it is independent of the species selected initially to be preserved in r_P for the derivation. While these features are not essential in studying first-order kinetics, they do expedite the analysis for second-order and third-order reaction systems discussed in Chapters Two and Three.

Effectiveness Factors

Effectiveness factors are commonly used to compare the average rate of reaction actually achieved to that possible in the absence of concentration gradients. Three types are encountered: the internal effectiveness factor, η_{int}, the external effectiveness factor, η_{ext}, and the overall effectiveness factor, $\eta_{overall} = \eta_{int}\eta_{ext}$. Only two need be considered at a time, and these will be $\eta_{overall}$ and η_{int}. The internal effectiveness factor gives the ratio of the average reaction rate within the slab relative to the reaction rate at the exposed surface, Lee (1985)

$$\eta_{int} = \frac{(1/L)\int_0^L r_P(x)dx}{r_{Ps}} = \frac{D_i\left(\dfrac{d\hat{c}_i}{dx}\right)_{x=L}}{Lr_{Ps}} \qquad 1.38$$

for the slab problem. The dimensionless problem, such as eq. (1.26), is still a slab problem, with $D = L = 1$, so

$$\eta_{int} = \frac{\int_0^1 r''_P(z)dz}{r''_P(z=1)} = \frac{\left(\dfrac{dc''}{dz}\right)_{z=1}}{r''_P(z=1)} \qquad 1.39$$

where r''_P is the dimensionless rate expression obtained after applying eqs. (1.19) and (1.20) to r_P. Using eq. (1.31) with eq. (1.26) gives

$$\eta_{int} = \frac{\mp\sqrt{2c''(0) - \Phi^2_{1st}c''(0)^2}}{-1} \qquad 1.40$$

for the first-order problem, again showing the need for the negative sign of the square root to obtain positive, or meaningful, internal effectiveness factors when using c''. Substitution of eq. (1.32) for $c''(0)$ gives the more familiar result

$$\eta_{int} = \frac{\tanh(\Phi_{1st})}{\Phi_{1st}} \qquad\qquad 1.41$$

valid for both reversible and irreversible first-order reactions with the definition of Φ_{1st}^2 given in eq. (1.28). For the irreversible zeroth-order reaction discussed earlier the equivalent result is

$$\eta_{int} = 1 \qquad \Phi_k \leq 1 \qquad\qquad 1.42$$

$$\eta_{int} = \frac{1}{\Phi_k} \qquad \Phi_k \geq 1 \qquad\qquad 1.43$$

$$\Phi_k = L\sqrt{\frac{k}{2D\hat{c}_s}} \ . \qquad\qquad 1.44$$

Both the zeroth-order and first-order results share asymptotic behavior of unity for small Thiele moduli values of Φ_k or Φ_{1st}, and of $1/\Phi_k$ or $1/\Phi_{1st}$ for large Thiele moduli values. This will be discussed in the next section.

The overall effectiveness factor is identical to the internal effectiveness factor for the case of no external mass transfer resistance. When the Robin's boundary condition is required, the overall effectiveness factor is defined

$$\eta_{overall} = \frac{r_P(\hat{c}_{is}, \hat{c}_{js}, \ldots)}{r_P(\hat{c}_{if}, \hat{c}_{jf}, \ldots)} \cdot \eta_{int} = \eta_{ext}\eta_{int} = ? \frac{r''_P(c'' = 0)}{r''_P(c'' = c''_{fi})} \cdot \eta_{int} \qquad 1.45$$

$$\eta_{overall} = ? \frac{(dc''/dz)_1}{r''_P(c'' = c''_{fi})} \cdot \qquad 1.46$$

The subscript on c''_{fi}, the dimensionless free stream concentration of i, is required, since the relationships used to eliminate $\hat{c}_j$ from the reaction rate expression to form r''_P are valid only within the slab and not in the free stream fluid. To use the last part of eq. (1.45) or to use eq. (1.46) requires more than just considerable care in writing r''_P. The overall effectiveness factor remains species independent, because the numerical values of the $r''_P(c''_{fi})$ are the same for each i, even though the expression for r''_P in the free stream must be modified for each species. This ultimately is due to the species' concentrations being interrelated through ratios of mass transfer coefficients instead of ratios of diffusivities between the free stream and the slab surface. This will be illustrated for the first-order Robin's problem. For the irreversible first-order problem, note that

$$Bi_{mA} c''_{fA} = \left(\frac{dc''}{dz}\right)_{z=1} = -\eta_{int} \qquad 1.47$$

and, since there is no second species to confuse the issue, $r''_P(c''_{fA}) = \Phi^2_{1st} c''_{fA} - 1$, both inside and outside the slab, so

$$\eta_{overall} = \frac{Bi_{mA} c''_{fA}}{\Phi^2_{1st} c''_{fA} - 1} \qquad\qquad 1.48$$

or

$$\frac{1}{\eta_{overall}} = \frac{\Phi^2_{1st}}{Bi_{mA}} - \frac{1}{Bi_{mA} c''_{fA}} = \frac{\Phi^2_{1st}}{Bi_{mA}} + \frac{1}{\eta_{int}} . \qquad\qquad 1.49$$

This sum of resistances format is discussed in Aris, p. 107 (1975). For the reversible first-order reaction, the expression, $r''_P(c''_{fA}) = \Phi^2_{1st} c''_{fA} - 1$, does not express the dimensionless reaction rate in the free stream nor does $r''_P(c''_{fB}) = \Phi^2_{1st} c''_{fB} - 1$, since both expressions contain no information about the relative rates of external mass transfer. Both expressions implicitly contain the effect of external mass transfer only for the selected species. The primary use of eqs. (1.45) and (1.46) in this work will be for single species reactions. A general expression for reactions with more than one species requires a new derivation beginning with the definition of the overall effectiveness factor in terms of a ratio of the dimensional reaction rate expressions, rather than the dimensionless reaction rate expressions in eq. (1.45). This will be discussed in Chapter Four.

The Generalized Thiele Modulus

In the above section, it was noted that the zeroth-order and first-order internal effectiveness factors were both asymptotic to unity and $1/\Phi$. This was not entirely accidental. The factor of two in Φ_k^2 permits this match. In 1965 the three independent authors, Aris, Bischoff, and Petersen, developed defining relations for an arbitrary reaction rate expression that would produce a generalized Thiele modulus, Φ_G, such that η_{int} would be asymptotic to unity and $1/\Phi_G$,

$$\Phi_G \equiv \frac{L r_P(\hat{c}_s)}{\sqrt{2 \int_{\hat{c}_{eq}}^{\hat{c}_s} D_e(\alpha) \, r_P(\alpha) \, d\alpha}}$$

1.50

see Lee (1985), where r_P has been rendered in terms of a single species through relations like eq. (1.20) to permit integration. The lower integration limit, $\hat{c}_{eq}$, is zero for an irreversible reaction, and a sensibly chosen zero of $r_P(\hat{c}) = 0$ for a reversible reaction, usually the one closest to $\hat{c}_s$. The two moduli derived so far, Φ_k and Φ_{1st}, are also generalized Thiele moduli for the zeroth-order and first-order reaction respectively.

Second-order and third-order power law kinetics for irreversible single species reactions have been investigated in the context of traditional and generalized Thiele moduli as part of studies on general n-th order kinetics

$$D \frac{d^2 \hat{c}}{dx^2} = k \hat{c}^n .$$ 1.51

It should be noted that the stoichiometric coefficient is neglected in writing the right-hand side. This gives rise to no problem for single species reactions where it can be assumed to be absorbed into the rate constant, k, although it is a little careless. Because this work deals with many multiple species reactions, the stoichiometric coefficients will always be indicated except when discussing earlier work. Making eq. (1.51) dimensionless with the slab half-width, L, and surface concentration, $\hat{c}_s$, leads to the traditional moduli

$$\Phi_{nA}^2 = \frac{L^2 k \hat{c}_s^{n-1}}{D} .$$ 1.52

The generalized moduli are very similar in form, needing only an appropriate scaling term to produce the desired asymptotic behavior

$$\Phi_G^2 = \left(\frac{n+1}{2} \right) \left(\frac{L^2 k \hat{c}_s^{n-1}}{D} \right) .$$ 1.53

The generalized moduli for n = 0,1,2,3 are given by

$$\Phi_G^2 = \frac{L^2 k}{2 D \hat{c}_s} \qquad n = 0$$ 1.54

$$\Phi_G^2 = \frac{L^2 k}{D} \qquad n = 1$$ 1.55

$$\Phi_G^2 = \frac{3L^2k\hat{c}_s}{2D} \qquad n = 2 \qquad\qquad 1.56$$

$$\Phi_G^2 = \frac{2L^2k\hat{c}_s^2}{D} \qquad n = 3 \qquad\qquad 1.57$$

These four irreversible reaction systems will be used throughout as a basis for comparison with results obtained later for second-order and third-order reaction systems. Plots of η_{int} versus Φ_G for these values of n date to Bischoff (1965) who determined the curves for n = 2 and n = 3 by numerical integration of the reaction-diffusion equation. Figure 3 is a plot of this type generated from analytical solutions derived as part of this work. The figure is in general agreement with Bischoff's plot as well as one in Aris' book (1975), but these tend to lose the feature that the curve for n = 2 is closer to the curve for n = 3 then to the curve for n = 1 over the full range of Φ_G.

In the context of the generalized modulus one can say that, at fixed Φ_G, a reaction giving results similar to those for first-order is less efficient than irreversible zeroth-order reactions but more efficient than irreversible second-order or third-order power law reactions. In other words, every physical single reaction system, either irreversible or reversible, has a location on Figure 3, Φ_G and η_{int}, which can be compared to n-th order behavior. This is perhaps the only setting in which diverse reaction kinetics can be readily compared. There is one further note concerning Figure 3. It is common to refer to the region $\Phi_G < 3$ as the region of negligible diffusion effects, $\eta_{int} \approx 1$, and to the region $\Phi_G > 4$ as the region of diffusion control, i.e. insensitive to the rate expression
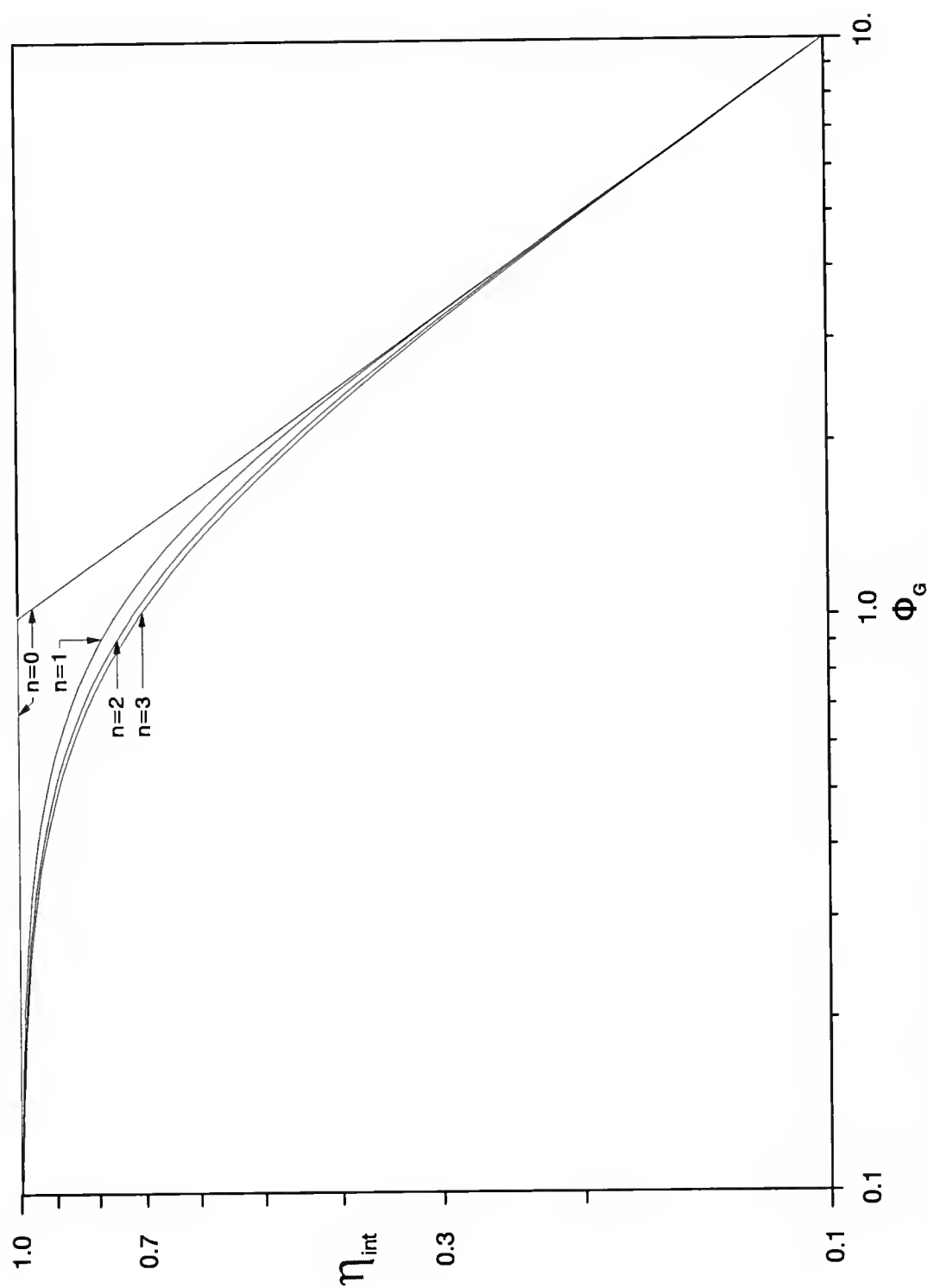
Figure 1.3 The Internal Effectiveness Factor for Simple Integer Power Law Kinetics.

form. It is not common, and also not wise, to base these distinctions upon c''(0), since it may be possible in some systems to have c''(0) small and η_{int} large. The asymptotic behavior with respect to Φ_G is guaranteed, although anything is possible between the asymptotes. This is amply demonstrated in the literature for n < 0 power law kinetics, for nonisothermal exothermic reactions, and even certain types of Langmuir-Hinshelwood kinetics. Results for most Langmuir-Hinshelwood kinetic expressions, however, lie between the curves for n = 0 and n = 2 in Figure 3.

Shape Factor Normalizations

Zeroth-order and first-order solutions have been derived in cylindrical and spherical coordinates, as well as some two-dimensional and three-dimensional geometries. Previous workers have found that a characteristic length choice of V_p/S_{ext}, the particle volume divided by the external surface area, brings first-order internal effectiveness factor solutions for slab, cylinder and sphere into approximate agreement, i.e. about as close as the curves for n = 1,2,3 in Figure 3. There is excellent asymptotic agreement and approximate agreement between the asymptotes. A more sophisticated renormalization was proposed by Miller and Lee, (1983). The potential of shape factor normalization has been somewhat neglected, since analytical solutions existed for zeroth-order and first-order reactions in many geometries, making shape factor normalization unnecessary, while there were virtually no other analytical solutions in any geometry. This work presents a very large number of new analytical solutions in the slab geometry for which there are no corresponding solutions in any other geometry. An opportunity

exists to extend these new solutions to other geometries at least approximately using the established principles of shape factor normalization.

Summary and Goals

Ideal catalysts would always have high internal effectiveness factors. A new catalyst of arbitrary geometry can be compared to an equivalent slab through shape factor normalization. The internal effectiveness factor of the slab can be calculated numerically, estimated from a graph such as Figure 3, or calculated from an analytical solution. Such procedures are facilitated by having a large library of analytical solutions available, but this has not been the case. Analytical solutions for the internal effectiveness factor exist for n = 0 and n = 1, as well as one for n = -1 in terms of Dawson's integral, Aris (1975), plus Thiele's solution for n = 2 power law kinetics which is

$$\eta_{int} = \sqrt{\frac{2D}{3L^2 k \hat{c}_s}\left[1 - \left(\frac{\hat{c}_0}{\hat{c}_s}\right)^3\right]}$$

1.58

where $\hat{c}_0 = \hat{c}(x=0)$ is obtained from the solution of either

$$\sqrt{\frac{L^2 k \hat{c}_s}{D}} = \sqrt[4]{\frac{3}{4}}\left\{F\left[\sin^{-1}\left(\frac{\sqrt{4\sqrt{3}(\hat{c}_s - \hat{c}_0)/\hat{c}_s}}{\sqrt{3} - 1 - \hat{c}_s/\hat{c}_0}\right), \sin(15°)\right]\right\}$$

1.59

for $\hat{c}_s/\hat{c}_0 < 1 + \sqrt{3}$, or

$$\sqrt{\frac{L^2 k \hat{c}_s}{D}} = \sqrt[4]{\frac{3}{4}}\left\{2K(15°) - F\left[\sin^{-1}\left(\frac{\sqrt{4\sqrt{3}(\hat{c}_s - \hat{c}_0)/\hat{c}_s}}{\sqrt{3} - 1 + \hat{c}_s/\hat{c}_0}\right), \sin(15°)\right]\right\} \quad 1.60$$

for $\hat{c}_s/\hat{c}_0 > 1 + \sqrt{3}$, where $\hat{c}_0$ is the dimensional midplane concentration, F is the elliptic integral of the first kind, and K is the complete elliptic integral of the first kind. Thiele's original notation was modified to conform with that used throughout this text. Thiele did not include an expression for $\hat{c}(x)$, which presumably would be similar to eqs. (1.59) and (1.60) with $\hat{c}(x)$ replacing $\hat{c}_0$ in one or more places, plus an appearance by x perhaps replacing L. Eqs. (1.59) and (1.60) are awkward in appearance, require two different elliptic integrals to evaluate, are each valid over only a specified, but implicit range, and are algebraically implicit in solution character since $\hat{c}_0$ is an unknown value of the solution which is needed in eq. (1.58) to determine η_{int}. The extension of this solution method to other second-order kinetic systems may be possible, but has not been studied by others as far as is known by the author. It may well be that this result discouraged other engineers from attempting to solve more complicated second-order kinetic reaction and diffusion problems. Nevertheless, one can hardly expect to solve a nonlinear second-order differential equation without at least having to evaluate one nonlinear algebraic expression to satisfy the boundary conditions. The following chapters will deal with the solution of the two problems

$$\frac{d^2\hat{c}}{dx^2} = a_2\hat{c}^2 + a_1\hat{c} + a_0 \qquad\qquad 1.61$$

and

$$\frac{d^2\hat{c}}{dx^2} = a_3\hat{c}^3 + a_2\hat{c}^2 + a_1\hat{c} + a_0 \qquad\qquad 1.62$$

derived from net second-order and third-order reversible and irreversible elementary reaction rate laws using the interrelationships between species developed earlier and using both the Dirichlet boundary conditions and the Robin's boundary conditions. Analytical solutions for the concentration profiles will be derived that are valid throughout the allowable parameter ranges without using elliptic integrals. The solution procedure will require determination of the midplane concentration in an implicit equation to satisfy one boundary condition. This single implicit step will complete the concentration profile equation as well as giving the internal effectiveness factor, which is a simple function of the Thiele moduli and the midplane concentration. Thus the new solutions will be more compact and easier to compute than Thiele's solution for $n = 2$ power law kinetics, as well as covering a much broader range of kinetic diversity.

CHAPTER 2
CONVENTIONAL SECOND-ORDER REACTION SYSTEMS

Overview of Second-Order Reaction and Diffusion

Limited work exists in the literature on the analysis of isothermal, coupled steady-state second-order reaction and diffusion problems. Several specific types of kinetics and physical configurations have been studied, and the results are summarized nicely by Aris (1975). This chapter will accomplish several interrelated goals. The conventional second-order reactions, those which are irreversible, reversible with another second-order reaction, and reversible with a first-order reaction, will be analyzed. The analysis in this chapter will be limited to the Dirichlet problem for a slab. This will lead to equations interrelating the individual species' concentrations as well as to an analysis of the minimum number of parameters needed to formulate a single general problem. This general reaction diffusion problem will be solved analytically for the dimensionless concentration profile with the aid of the Weierstrass elliptic Pe-function, $\wp$, in terms of just two parameters. Three different dimensionless concentrations will be used to facilitate different stages of the development. While this is a little awkward, each has its advantages and disadvantages. These will be discussed. The mathematical nature of the Weierstrass elliptic Pe-function will be outlined. The general nonlinear governing differential equation leads to an implicit algebraic expression to be solved to satisfy one

boundary condition. The dependence of the solution of this equation on the two parameters will be examined. Second-order reactions reversible with another second-order reaction possess a special feature. Under certain values of the kinetic rate constants and diffusivities, the governing differential equation will degenerate to first-order kinetics with linear differential equations. This could be forced to occur in many instances by adjusting temperature, for example, without invoking any infinite diffusivities or other asymptotic limits. Finally, an analytical expression for the internal effectiveness factor will be examined as a function of the two most fundamental parameters.

Burghardt's recent article (1990) still claims that there is a lack of an explicit relationship between the internal effectiveness factor of a pellet and the characteristic parameters for other than zeroth-order and first-order reactions. Burghardt uses theorems from singularity theory to divide the feasible parameter space into regions with different bifurcation diagrams, i.e. with different numbers of possible solutions, for an exothermic reversible first-order reaction with a uniform pellet temperature different from that in the surrounding fluid. Their analysis should now be possible for selected second-order kinetic cases. Relationships between the internal effectiveness factor and the new analytical solution will be derived here for seven classes of second-order kinetics. Analytical solutions for second-order kinetic expressions are generally only possible for Cartesian coordinates and then only in terms of elliptic functions or integrals. These are either sufficiently unusual or unavailable that many engineers would undertake a numerical solution of the problem instead. This need not be the case as will be shown

below. Furthermore, a calculated concentration profile is not required to determine the internal effectiveness factor. The internal effectiveness factor can be calculated if the midplane concentration alone is known.

As will be seen below, the initial dimensionless forms of the individual species' governing equations need contain no more parameters than the number of distinct species in the elementary reaction plus one for the Dirichlet problem, i.e. up to five for the most general second-order reversible case, $A + B \rightleftarrows P + R$. The number of dimensionless groups contracts to just three species' dependent parameters in the first step of the new analytical solution procedure for the dimensionless concentration profile (fewer for irreversible reaction cases).

The analytical solutions derived in this chapter contain an expansion in terms of the Weierstrass elliptic Pe-function that is arguably easier to use than those for the traditionally acceptable first-order irreversible reaction in an infinite cylinder, which requires the modified Bessel function of the first kind.

Some earlier analyses exist in the literature for simultaneous second-order reactions and diffusion, Thiele (1939), Maymo (1966), Bailey (1971), Tartarelli (1970). The previous analyses have not produced much general theory about second-order elementary reactions. These early analyses have tended to be in the spherical coordinate system of catalyst pellets and have relied heavily on numerical methods to obtain solutions. Often these authors have invoked stoichiometric surface concentrations and/or a common diffusivity for all species to reduce the dimensionality of the parameter space in order to permit graphical presentation of the results. Indeed, one recurring problem

in previous presentations of solution results for simultaneous diffusion and second-order kinetics has been the confusion in identifying the minimum dimension of its parameter space. Among these earlier analyses are some with up to eight dimensional parameter spaces. The first step reduction of the governing equations taken in this chapter produces a three-parameter basis for isothermal reaction kinetics with second-order forward reactions, and either second-, first-, zeroth-order or no reverse reactions (nine kinetic schemes are possible, counting two with zeroth-order reverse reactions). Numerical values of the three parameters depend on the species selected for the calculation. This is not a major drawback, but it can be inconvenient. All three parameters are nonzero except when, (1) a special first-order degeneracy occurs, (2) the surface concentrations reflect complete or equilibrium conversion, or (3) the reaction is irreversible ($2A \rightarrow$ products and $A + B \rightarrow$ products).

Further analysis of this problem yields a two-parameter basis which is independent of the chemical species selected for the derivation. These two parameters are considered to contain the essence of second-order reaction and diffusion behavior. A clear picture has emerged with respect to the conditions under which the general second-order reversible reaction system is free from diffusion limitations or is diffusion limited as a result of the reduction to two parameters. Also emerging later in this chapter will be some less obvious results. These include the manner in which the internal effectiveness factor is affected by the two parameters, bounds on the dimensionless midplane concentration and its estimation, a bound on the relative magnitudes of the two

parameters and asymptotic behavior of the internal effectiveness factor as a function of the two parameters.

Some additional practical problems have been studied by others. These will be briefly summarized here. Bailey (1971) has analyzed the problem of optimum surface concentration for the irreversible reaction case $A + B \rightarrow$ products, when the diffusivities are unequal. Tarterelli et al. (1970) have studied the two irreversible kinetic cases in a macropore-micropore catalyst model. Thiele (1939) developed an analytic solution for the slab midplane concentration and internal effectiveness factor for the single species' irreversible reaction, $2A \rightarrow$ products, using elliptic integrals instead of elliptic functions; see Chapter One. The selectivity of porous catalysts undergoing parallel reactions was examined by Roberts (1972), and includes second-order reactions in parallel with either a zeroth-order or first-order reaction. Roberts also used elliptic integrals. Two early studies on nonisothermal behavior are noteworthy in that the authors disagree on the results obtained, Tinkler and Metzler (1961) and Petersen (1962). These earlier studies as well as this study neglect the effect of volume change during reaction, which is most often valid when the system concentrations remain near those at the surface, when the effective diffusivity is predominantly due to Knudsen diffusion, or when the fluids are dilute gases in an inert gas solvent or liquids.

Governing Equations and Dimensionless Groups

Consider the general second-order reversible isothermal reaction of the type $A + B \rightleftarrows P + R$, occurring in a slab-like medium or along the axis of a cylinder as

illustrated in Chapter One, under the assumption of constant effective diffusivity, D_i.

The governing equations take the following form

$$D_A \frac{d^2 \hat{c}_A}{dx^2} = -r_P \qquad D_P \frac{d^2 \hat{c}_P}{dx^2} = r_P$$

$$D_B \frac{d^2 \hat{c}_B}{dx^2} = -r_P \qquad D_R \frac{d^2 \hat{c}_R}{dx^2} = r_P$$

2.1

where $r_p = k_r \hat{c}_P \hat{c}_R - k_f \hat{c}_A \hat{c}_B$ and x is measured out from the slab midplane. These

expressions can be written more generally as

$$D_i \frac{d^2 \hat{c}_i}{dx^2} = v_i r_P$$

2.2

The rate of product formation rate expressions, r_P, considered in this chapter are given

in Table 2.1. The first seven stoichiometries listed there are discussed in this chapter.

Zeroth-order reverse reactions are not discussed here. The analysis that follows always

assumes a symmetric problem, i.e. the slab with sealed midplane or the slab with two

exposed faces with identical surface conditions. This leads to either a Dirichlet or

Robin's problem at the exposed surface. The Dirichlet problem is the more basic of the

two. Generally a solution can be found for the corresponding Robin's problem, if the

Dirichlet problem can be solved.

There are many steps between this point and the analytical solution. The solution

strategy to be employed will be outlined here so the reader knows what to expect in the

pages ahead. The initial step will be to take a set of n coupled nonlinear ordinary

Table 2.1 Typical Second-Order Kinetic Schemes

Case	Stoichiometry	Rate Expression
I	$A + B \rightleftarrows P + R$	$r_P = k_r \hat{c}_P \hat{c}_R - k_f \hat{c}_A \hat{c}_B$
II	$A + A \rightleftarrows P + R$	$r_P = k_r \hat{c}_P \hat{c}_R - k_f \hat{c}_A^2$
III	$A + A \rightleftarrows P + P$	$r_P = k_r \hat{c}_P^2 - k_f \hat{c}_A^2$
IV	$A + B \rightleftarrows P$	$r_P = k_r \hat{c}_P - k_f \hat{c}_A \hat{c}_B$
V	$A + A \rightleftarrows P$	$r_P = k_r \hat{c}_P - k_f \hat{c}_A^2$
VI	$A + B \rightarrow$	$r_P = - k_f \hat{c}_A \hat{c}_B$
VII	$A + A \rightarrow$	$r_P = - k_f \hat{c}_A^2$
VIII	$A + B \rightleftarrows$ zeroth-order	$r_P = k_r - k_f \hat{c}_A \hat{c}_B$
IX	$A + A \rightleftarrows$ zeroth-order	$r_P = k_r - k_f \hat{c}_A^2$

differential equations (ODE's) and form n single species ODE's, where n is the number of species appearing in the rate expression. These uncoupled ODE's will be made dimensionless using a characteristic length and the species' surface concentrations. It will be prudent at this point to condense and label numerous common dimensionless groups contained in the ODE's to simplify notation. The fourth step is an optional step as far as obtaining the analytical solution is concerned. A properly chosen linear transformation of the dimensionless species concentrations leads to a species independent ODE containing fewer parameters which are themselves independent of species in the sense that they are identical regardless of which species is used as a starting point for the transformation. The variables are separated and integrated one time by conventional methods in the fifth step, see Lee (1985), leading to a concentration polynomial one degree higher than in the original reaction rate expression. Sixth, take a complete, or entire, Taylor series expansion of this polynomial about one of its zeros (no truncations). Next, make a very special and particular nonlinear transformation of the concentration variable. Then separate variables for the second time and recognize that the result is something with particular significance, i.e. the Weierstrass elliptic Pe-function. Finally, back substitute to whatever point desired to produce dimensionless or dimensional concentration profile equations.

This chapter will consider the Dirichlet problem. Conventional boundary conditions for the Dirichlet problem are

$$\hat{c}_i = \hat{c}_{is} \qquad x = L \qquad\qquad 2.3$$

$$\frac{d\hat{c}_i}{dx} = 0 \qquad x = 0. \qquad\qquad 2.4$$

The following relationships between the species are readily derivable from the governing equations, see Chapter One, since $(D_i\hat{c}_i/v_i - D_j\hat{c}_j/v_j)$ are solutions of a potential function, regardless of the coordinate system chosen, and thus equal to a constant. For the Dirichlet problem, this constant is known from the surface condition, i.e.

$$D_A\hat{c}_A - D_B\hat{c}_B = D_A\hat{c}_{As} - D_B\hat{c}_{Bs} \qquad\qquad 2.5$$

$$D_A\hat{c}_A + D_P\hat{c}_P = D_A\hat{c}_{As} + D_P\hat{c}_{Ps} \qquad\qquad 2.6$$

and similarly for R as for P. These can also be written more generally as

$$\frac{D_i}{v_i}(\hat{c}_i - \hat{c}_{is}) = \frac{D_j}{v_j}(\hat{c}_j - \hat{c}_{js}) . \qquad\qquad 2.7$$

These expressions are critical to continuing the analysis for nonlinear kinetic rate equations. All but one concentration can be eliminated from r_P using eq. (2.7). Then the system can be reduced to a single ordinary differential equation. If A is selected, and concentration and length are made dimensionless with $\hat{c}_{As}$ and L, then the above second-order reversible system reduces to

$$\frac{d^2 c_A}{dz^2} = \left(\frac{L^2 k_f \hat{c}_{As}}{D_B} - \frac{L^2 k_r D_A \hat{c}_{As}}{D_P D_R} \right) c_A^2 + \left(\frac{L^2 k_f \hat{c}_{Bs}}{D_A} - \frac{L^2 k_f \hat{c}_{As}}{D_B} + \right.$$

$$\frac{L^2 k_r \hat{c}_{Ps}}{D_R} + \frac{L^2 k_r \hat{c}_{Rs}}{D_P} + \frac{2 L^2 k_r D_A \hat{c}_{As}}{D_P D_R} \right) c_A - \left(\frac{L^2 k_r \hat{c}_{Ps} \hat{c}_{Rs}}{D_A \hat{c}_{As}} + \right. \qquad 2.8$$

$$\left. \frac{L^2 k_r D_A \hat{c}_{As}}{D_P D_R} + \frac{L^2 k_r \hat{c}_{Ps}}{D_R} + \frac{L^2 k_r \hat{c}_{Rs}}{D_P} \right)$$

where $c_A = \hat{c}_A / \hat{c}_{As}$ and $z = x/L$. In spite of the lengthy coefficients, eq. (2.8) is an improvement over eq. (2.1). The right-hand side of this equation will be referred to as the diffusion modified reaction rate expression. Dimensionless species' solutions depend only on the values of the three coefficients of c_A^2, c_A and 1. The above equation can be written

$$\frac{d^2 c_A}{dz^2} = 6 a_{1A} c_A^2 + 6 a_{2A} c_A + 2 a_{3A} \qquad 2.9$$

with revised boundary conditions

$$c_A = 1 \qquad z = 1 \qquad 2.10$$

$$\frac{d c_A}{dz} = 0 \qquad z = 0 . \qquad 2.11$$

The numerical constants in eq. (2.9) are per Whittaker and Watson (1950) and, when following their solution method, these choices reduce the occurence of fractions in the

Table 2.2 Coefficients of c_i^2 for Second-Order Reactions

Case	Species	$6a_1$
I	A	$\Phi_{A+B}^2 - \Gamma_{AP}\Phi_{P+R}^2$
I	B	$\Phi_{B+A}^2 - \Gamma_{AP}\Phi_{B+A}^2\Phi_{P+R}^2/\Phi_{A+B}^2$
I	P	$\Phi_{P+R}^2 - \Phi_{A+B}^2/\Gamma_{AP}$
I	R	$\Phi_{R+P}^2 - \Phi_{A+B}^2\Phi_{R+P}^2/\Gamma_{AP}\Phi_{P+R}^2$
II	A	$2(\Phi_{2A}^2 - \Gamma_{AP}\Phi_{P+R}^2/4)$
II	P	$\Phi_{P+R}^2 - 4\Phi_{2A}^2/\Gamma_{AP}$
II	R	$\Phi_{R+P}^2 - 4\Phi_{2A}^2\Phi_{R+P}^2/\Gamma_{AP}\Phi_{P+R}^2$
III	A	$2(\Phi_{2A}^2 - \Gamma_{AP}\Phi_{2P}^2)$
III	P	$2(\Phi_{2P}^2 - \Phi_{2A}^2/\Gamma_{AP})$
IV	A	Φ_{A+B}^2
IV	B	Φ_{B+A}^2
IV	P	$-\Phi_{A+B}^2/\Gamma_{AP}$
V	A	$2\Phi_{2A}^2$
V	P	$-4\Phi_{2A}^2/\Gamma_{AP}$
VI	A	Φ_{A+B}^2
VI	B	Φ_{B+A}^2
VII	A	$2\Phi_{2A}^2$

Table 2.3 Coefficients of c_i for Second-Order Reactions

Case	Species	$6a_2$
I	A	$\Phi_{B+A}^2-\Phi_{A+B}^2+\Phi_{P+R}^2+\Phi_{R+P}^2+2\Gamma_{AP}\Phi_{P+R}^2$
I	B	$\Phi_{A+B}^2-\Phi_{B+A}^2+\Phi_{P+R}^2+\Phi_{R+P}^2+2\Gamma_{AP}\Phi_{B+A}^2\Phi_{R+P}^2/\Phi_{A+B}^2$
I	P	$\Phi_{R+P}^2-\Phi_{P+R}^2+\Phi_{A+B}^2+\Phi_{B+A}^2+2\Phi_{A+B}^2/\Gamma_{AP}$
I	R	$\Phi_{P+R}^2-\Phi_{R+P}^2+\Phi_{A+B}^2+\Phi_{B+A}^2+2\Phi_{B+A}^2\Phi_{R+P}^2/\Gamma_{AP}\Phi_{P+R}^2$
II	A	$\Phi_{P+R}^2+\Phi_{R+P}^2+\Gamma_{AP}\Phi_{R+P}^2$
II	P	$\Phi_{R+P}^2-\Phi_{P+R}^2+4\Phi_{2A}^2+8\Phi_{2A}^2/\Gamma_{AP}$
II	R	$\Phi_{P+R}^2-\Phi_{R+P}^2+4\Phi_{2A}^2+8\Phi_{2A}^2\Phi_{R+P}^2/\Gamma_{AP}\Phi_{P+R}^2$
III	A	$2(2\Phi_{2P}^2+2\Gamma_{AP}\Phi_{2P}^2)$
III	P	$2(2\Phi_{2A}^2+2\Phi_{2A}^2/\Gamma_{AP})$
IV	A	$\Phi_{B+A}^2-\Phi_{A+B}^2+\Phi_P^2$
IV	B	$\Phi_{A+B}^2-\Phi_{B+A}^2+\Phi_P^2$
IV	P	$\Phi_P^2+\Phi_{A+B}^2+\Phi_{B+A}^2+2\Phi_{A+B}^2/\Gamma_{AP}$
V	A	Φ_P^2
V	P	$\Phi_P^2+4\Phi_{2A}^2+4\Phi_{2A}^2/\Gamma_{AP}$
VI	A	$\Phi_{B+A}^2-\Phi_{A+B}^2$
VI	B	$\Phi_{A+B}^2-\Phi_{B+A}^2$
VII	A	0

Table 2.4 Constant Coefficients for Second-Order Reactions

Case	Species	$2a_3$
I	A	$-(\Phi_{R+P}^2+\Phi_{P+R}^2+\Gamma_{AP}\Phi_{P+R}^2+\Phi_{R+P}^2/\Gamma_{AP})$
I	B	$-(\Phi_{P+R}^2+\Phi_{R+P}^2+\Gamma_{AP}\Phi_{B+A}^2\Phi_{P+R}^2/\Phi_{A+B}^2+\Phi_{A+B}^2\Phi_{R+P}^2/\Gamma_{AP}\Phi_{B+A}^2)$
I	P	$-(\Phi_{A+B}^2+\Phi_{B+A}^2+\Gamma_{AP}\Phi_{B+A}^2+\Phi_{A+B}^2/\Gamma_{AP})$
I	R	$-(\Phi_{A+B}^2+\Phi_{B+A}^2+\Gamma_{AP}\Phi_{B+A}^2\Phi_{P+R}^2/\Phi_{R+P}^2+\Phi_{A+B}^2\Phi_{R+P}^2/\Gamma_{AP}\Phi_{P+R}^2)$
II	A	$-(\Phi_{P+R}^2+\Phi_{R+P}^2+2\Phi_{R+P}^2/\Gamma_{AP}+\Gamma_{AP}\Phi_{P+R}^2/2)$
II	P	$-\Phi_{2A}^2(4+\Gamma_{AP}+4/\Gamma_{AP})$
II	R	$-\Phi_{2A}^2(4+\Gamma_{AP}\Phi_{P+R}^2/\Phi_{R+P}^2+4\Phi_{R+P}^2/\Gamma_{AP}\Phi_{P+R}^2)$
III	A	$-2\Phi_{2P}^2(2+\Gamma_{AP}+1/\Gamma_{AP})$
III	P	$-2\Phi_{2A}^2(2+\Gamma_{AP}+1/\Gamma_{AP})$
IV	A	$-\Phi_P^2(1+1/\Gamma_{AP})$
IV	B	$-\Phi_P^2(1+\Phi_{A+B}^2/\Gamma_{AP}\Phi_{B+A}^2)$
IV	P	$-\Phi_{A+B}^2-\Phi_{B+A}^2-\Gamma_{AP}\Phi_{B+A}^2-\Phi_{A+B}^2/\Gamma_{AP}$
V	A	$-\Phi_P^2(1+1/\Gamma_{AP})$
V	P	$-\Phi_{2A}^2(4+\Gamma_{AP}+4/\Gamma_{AP})$
VI	A	0
VI	B	0
VII	A	0

final results. Six dimensionless groups appear naturally in these three coefficients in eq. (2.8). If B, P or R had been selected instead of A, then some of these groups and some new, but similar, groups would have appeared. Expressions for the a_{ij} are given by reaction and species in Tables 2.2-2.4 for the seven cases free of zeroth-order reactions using a notational standard described below.

A shorthand notation system would be useful to help minimize the number of dimensionless subgroups appearing within the more general parameters and facilitate studies of parameter interrelationships. After all, there are 17 species dependent ODE's under consideration at this point. Such a notational system should also retain some physical significance or familiarity. Toward this end, a set of irreversible reaction Thiele moduli will be defined

$$\Phi^2_{i+j} = L^2 k_i \hat{c}_{is} / D_j \qquad\qquad 2.12$$

where i,j are either both products or both reactants. The k_i indicate the rate constant, either k_f or k_r, multiplying the concentration of species I in the rate expression. Such a group would appear naturally in the study of the irreversible reaction I + J → products. Large values of such a group would suggest possible strong diffusional effects, while small values suggest a possibility of nearly diffusion free operation. The true state of affairs will be revealed by further analysis. If i = j, define the irreversible reaction Thiele modulus

$$\Phi^2_{2i} = L^2 k_i \hat{c}_{is} / D_i \qquad\qquad 2.13$$

which would arise in studying 2I → products or I + I → products, and define

$$\Gamma_{ij} = \frac{D_i \hat{c}_{is}}{D_j \hat{c}_{js}} \qquad\qquad 2.14$$

where i and j are not both products or both reactants. This ratio serves as a bridge between product and reactant species. The set $\{\Phi^2_{A+B},\ \Phi^2_{B+A},\ \Phi^2_{P+R},\ \Phi^2_{R+P},\ \Gamma_{AP}\}$ is sufficient, as can be seen from the tables, to write the dimensionless governing equations of all four species in the reaction $A + B \rightleftarrows P + R$. Another sufficient set $\{\Phi^2_{A+B},\ \Phi^2_{P+R},\ \Gamma_{AB},\ \Gamma_{AP},\ \Gamma_{AR}\}$ is prototypical of many similar sets, as is $\{k_f/k_r,\ \Phi^2_{A+B},\ \Gamma_{AB},\ \Gamma_{AP},\ \Gamma_{AR}\}$. The first set is also sufficient to express the internal effectiveness factor using the derivative of the dimensionless concentration. It can be seen in Table 2.2 that Φ^2_{i+j} is the coefficient of c^2_i when the rate constant of the opposing reaction is zero, and that it has similar dependence on physical parameters as the generalized Thiele modulus for a second-order irreversible reaction of a single species given in Bischoff (1965), Aris (1975), and Lee (1985)

$$\Phi^2_G = 3L^2 k \hat{c}_s / 2D \ . \qquad\qquad 2.15$$

The following interrelationships between the parameters in the new notational system should be noted

$$\Gamma_{ij} = 1/\Gamma_{ji} \qquad\qquad 2.16$$

$$\Gamma_{ik} = \left(\frac{\Phi^2_{i+j}}{\Phi^2_{j+i}} \right) \Gamma_{jk} \ . \qquad\qquad 2.17$$

For the case of mixed first-order and second-order reversible kinetics, a first-order irreversible reaction Thiele modulus will be defined in the traditional way as in Chapter One, $\Phi_i^2 = L^2 k_i/D_i$, where i indicates the species undergoing a first-order reaction and its rate constant. With this adopted nomenclature, the coefficients of the governing equations for many second-order systems can be readily condensed. Expansions for the coefficients, a_{ij}, for the first seven second-order kinetic expressions listed in Table 2.1, have been formulated in terms of the irreversible reaction Thiele moduli and a single Γ_{ij}. The results of employing the above nomenclature scheme are summarized in Tables 2.2-2.4, for $d^2 c_i/dz^2 = 6a_{1i} c_i^2 + 6a_{2i} c_i + 2a_{3i}$.

Second-order systems with a zeroth-order reverse reaction can be handled by the integration methods that follow, but are not considered in this chapter. In dealing with such reactions, it is potentially possible to associate a real species with the zeroth-order reaction, and to have the concentration of that species drop to zero at an intermediate point in the slab. This requires the introduction of an additional parameter to establish this position, and conventionally the rate constant for the zeroth-order step would have to be made zero or set equal to the opposing rate beyond that point of penetration.

<u>Solution of the Dirichlet Problem</u>

The 17 dimensionless species dependent governing equations in the above seven conventional cases are of the same form, namely

$$\frac{d^2 c_i}{dz^2} = 6\, a_{1i} c_i^2 + 6\, a_{2i} c_i + 2\, a_{3i} \qquad\qquad 2.18$$

where a_{1i}, a_{2i} and a_{3i} are those coefficients summarized in Tables 2.2-2.4.

Two generic ways are developed here to further unify the species dependent parameter problem of eq. (2.18) to a unified two-parameter boundary value expression for the general case where the a_{ij} are all nonzero. This step is not critical to solving the differential equation, but reducing the parameter space dimension is quite useful and well worth pursueing. For the first of these methods, let

$$c' = 6a_{1i}(c_i - 1) .$$

2.19

The variable, c', could also be interpreted as a dimensionless extent of diffusion reaction variable, since it characterizes the species independent evolution of the diffusion reaction and has the value of zero at the slab surface. The result that c' is indepenent of species is anticipated in leaving it unsubscripted. Then eq. (2.18) becomes

$$\frac{d^2c'}{dz^2} = c'^2 + (12a_{1i}+6a_{2i})c' + 6a_{1i}(6a_{1i}+6a_{2i}+2a_{3i})$$

2.20

which can be rewritten as

$$\frac{d^2c'}{dz^2} = c'^2 + \Phi_{1st}^2 c' + \Psi$$

2.21

with boundary conditions

$$c' = 0 \qquad at \qquad z = 1$$

2.22

$$\frac{dc'}{dz} = 0 \qquad at \qquad z = 0$$

2.23

where $\Phi_{1st}^2 = 12a_{1i} + 6a_{2i}$ and $\Psi = 6a_{1i}(6a_{1i} + 6a_{2i} + 2a_{3i})$. The sign of c' is no longer necessarily positive, unlike the case for c_i in eq. (2.18). The scaling choice made in eq. (2.19) leads to a coefficient of unity for c'^2. Other scaling choices are possible that would lead to a fixed coeffient other than unity for c'^2, but they do not seem to offer any particular advantages.

The procedure for the first integration of the general ordinary differential equation above is well known; see Lee (1985). Let q = dc'/dz, then

$$\frac{dq}{dz} = c'^2 + \Phi_{1st}^2 c' + \Psi \ . \qquad\qquad 2.24$$

Multiply both sides by 2qdz, equivalent to 2dc', and integrate to obtain

$$q^2 = \frac{2}{3}c'^3 + \Phi_{1st}^2 c'^2 + 2\Psi c' + \alpha \qquad\qquad 2.25$$

where α is an undetermined constant of integration. It is possible to substitute the definition of q, separate variables, choose integration limits, etc. at this point, but the analytical solution of that integral would not be known. Note that q(c'(0)) = 0 by the boundary conditions. This establishes a relationship between α and c'(0), namely

$$\alpha = -\frac{2}{3}c'(0)^3 - \Phi_{1st}^2 c'(0)^2 - 2\Psi c'(0) \ . \qquad\qquad 2.26$$

The value of q(1) will be needed later for determining the internal effectiveness factor which depends on the surface concentration gradient. It is given by

$$q(1) = \pm\sqrt{\alpha} = \pm\sqrt{-\frac{2}{3}c'(0)^3 - \Phi_{1st}^2 c'(0)^2 - 2\Psi c'(0)} \qquad\qquad 2.27$$

where the same sign as Ψ is generally correct physically. If a reliable estimate of c'(0) is available, and concentration profiles are not required, then it is possible to avoid performing the second integration, and to proceed directly to the calculation of the internal effectiveness factor. Assuming the contrary, it is important to recall that c'(0) is a root of $q^2(c'(0))$, since $(c'^n - c'(0)^n) = (c' - c'(0))$ times a (polynomial of order n-1) for all relevant n in this study, CRC Standard Mathematical Tables, (1975). The fact that the remaining boundary condition is at $z = 1$, not at $z = 0$, must be temporarily ignored in the following steps. First expand $q^2(c')$ about $q^2(c'(0))$ in a Taylor series.

$$q^2(c') = (2c'(0)^2 + 2\Phi_{1st}^2 c'(0) + 2\Psi)(c' - c'(0)) + \\ (4c'(0) + 2\Phi_{1st}^2)(c' - c'(0))^2 + 4(c' - c'(0))^3 \qquad 2.28$$

Note that this equation is complete, and not an approximation, since eq. (2.25) is a cubic polynomial. The point of this step is to eliminate, or at least disguise, the constant term with c'(0) in eq. (2.25) by moving it into the differences with c'. Then define

$$q^2(c') \equiv 4A_3(c' - c'(0)) + 6A_2(c' - c'(0))^2 + 4A_1(c' - c'(0))^3 . \qquad 2.29$$

Substitute dc'/dz for q, separate the variables c' and z, and then take the integral from (0, c'(0)) to (z, c').

$$\int_0^z dz = \int_{c'(0)}^{c'} \frac{d\alpha}{\sqrt{4A_3(\alpha - c'(0)) + 6A_2(\alpha - c'(0))^2 + 4A_1(\alpha - c'(0))^3}} \qquad 2.30$$

Make a change of variables to $\tau = (\alpha - c'(0))^{-1}$:

$$z = \int\limits_{\tau}^{\infty} \frac{d\tau}{\sqrt{4A_3\tau^3 + 6A_2\tau^2 + 4A_1\tau}} \ . \qquad 2.31$$

Note that if the original kinetics had been third-order in c', it would only have added a constant term to the quantity in brackets, which would have been called A_0; see Chapter Three. This is therefore a powerful substitutiton, which is not fully exploited here but will be in Chapter Three. The next substitution is conventional and simultaneously reduces the coefficient of the cubic term to four and eliminates the quadratic term. Let $\sigma = A_3\tau + A_2/2$, then

$$z = \int\limits_{\sigma}^{\infty} \frac{d\sigma}{\sqrt{4\sigma^3 - (3A_2^2 - 4A_1A_3)\,\sigma - (2A_1A_2A_3 - A_2^3)}} \qquad 2.32$$

$$z \equiv \int\limits_{\sigma}^{\infty} \frac{d\sigma}{\sqrt{4\sigma^3 - g_2\sigma - g_3}} \ . \qquad 2.33$$

The numbers, g_2 and g_3, are *invariants* of the original third-order polynomial, Whittaker and Watson (1950), and are also (and more readily) given by

$$g_2 = \frac{(\Phi_{1st}^4 - 4\Psi)}{12} \qquad 2.34$$

$$g_3 = \frac{4c'(0)^3 + 6\Phi_{1st}^2 c'(0)^2 + 12\Psi c'(0) + 6\Phi_{1st}^2\Psi - \Phi_{1st}^6}{216}. \qquad 2.35$$

The relationship between α and c'(0) is needed to verify the g_3 equivalence. The invariant, g_2, is independent of c'(0) and therefore *ab initio* known.

Eq. (2.33) is one defining relation of the Weierstrass elliptic Pe-function. It is also written with an elaborate script capital P, $\wp$, Whittaker and Watson (1950). The variable transformations following eq. (2.30) were made with this end in mind. The cubic polynomial in the denominator will be referred to as the canonical polynomial of the problem, even though it is not quite the canonical form of a cubic polynomial given in most mathematical handbooks. These lack the factor of four and use addition rather than subtraction of the lower order terms. The defining relation for the Weierstrass elliptic Pe-function translates eq. (2.33) to

$$\sigma = \wp(z; g_2, g_3) \, . \qquad\qquad 2.36$$

Substituting τ for σ and then c' for τ gives the analytical solution for the dimensionless concentration profile in terms of the still undetermined midplane concentration

$$c'(z) = c'(0) + \frac{6(c'(0)^2 + \Phi_{1st}^2 c'(0) + \Psi)}{12\,\wp(z; g_2, g_3) - 2c'(0) - \Phi_{1st}^2} \qquad\qquad 2.37$$

where c'(0) must be evaluated from eq. (2.37) using the boundary condition of eq. (2.22). Eq. (2.37) can be inserted into eq. (2.19) to give the dimensionless species concentration profiles.

An alternative approach, Chapter One, to reducing eq. (2.18) is to take

$$c'' = \frac{1 - c_i}{6a_{1i} + 6a_{2i} + 2a_{3i}} = \frac{-c'}{\Psi} \qquad\qquad 2.38$$

or equivalently in terms of original problem parameters

$$c'' = \frac{D_i(\hat{c}_{is} - \hat{c}_i)}{L^2 v_i r_{Ps}}$$

2.39

where r_{Ps} is r_P evaluated at the surface concentrations. This leads to the following revised governing equation

$$\frac{d^2c''}{dz^2} = -\Psi c''^2 + \Phi_{1st}^2 c'' - 1$$

2.40

where Φ_{1st} and Ψ are identical with those defined by eqs. (2.20) and (2.21). The boundary conditions for c'' are identical with those for c'. The analytical solution for eq. (2.40) is derived exactly as eq. (2.37) and is given by

$$c''(z) = c''(0) + \frac{6(-\Psi c''(0)^2 + \Phi_{1st}^2 c''(0) - 1)}{12 \wp(z; g_2, g_3) + 2\Psi c''(0) - \Phi_{1st}^2}$$

2.41

with invariants

$$g_2 = \frac{(\Phi_{1st}^4 - 4\Psi)}{12}$$

2.42

$$g_3 = \frac{-4\Psi^3 c''(0)^3 + 6\Psi^2 \Phi_{1st}^2 c''(0)^2 - 12\Psi^2 c''(0) + 6\Psi \Phi_{1st}^2 - \Phi_{1st}^6}{216}$$

2.43

The same results could be obtained by direct substitution of eq. (2.38) into eqs. (2.34), (2.35) and (2.37). The numerical values of the two invariants are unaffected by the change of variables. The integration technique could have been applied to the original ODE with three parameters as well. Remember that the reduction to two parameters was not required to solve the ODE. Interested readers may consult Koopman and Lee, 1991, where this form is derived in full. Inclusion of this integration is redundant in this chapter, and the three-parameter form is also less useful for what follows with regard to second-order reaction and diffusion systems than the two-parameter form. Using either eq. (2.37) or eq. (2.41), it is now possible to present general solutions for internal effectiveness factors, slab midplane concentrations, etc. as functions of Φ_{1st} and Ψ.

The Two Fundamental Parameters

The two fundamental parameters, Φ_{1st}^2 and Ψ, have significance beyond reducing the problem from one with three parameters, the a_{ij}, to one with two parameters. The first of these parameters, Φ_{1st}^2 is never negative and is numerically independent of the species chosen in the derivation. As seen in Table 2.5, it takes the form of a sum of irreversible reaction Thiele moduli, i.e. moduli that one would derive from each species' governing equation by ignoring reverse reactions

$$\Phi_{1st}^2 = \sum_{all\ i} (v_i\, \Phi_{for\ i})^2 \qquad\qquad 2.44$$

where the sum is over all species, and $\Phi_{for\ i}$ is either Φ_{i+j}, Φ_{2i}, or Φ_i depending on the kinetics. This expression is reminiscent of the one for the Thiele modulus of a first-order

Table 2.5 Defining Relations for the Parameters of the Governing Equations for Seven Second-Order Reaction Systems

Case	Φ^2_{1st}	Ψ
I	$\Phi^2_{A+B}+\Phi^2_{B+A}+\Phi^2_{P+R}+\Phi^2_{R+P}$	$\Phi^2_{A+B}\Phi^2_{B+A}+\Phi^2_{P+R}\Phi^2_{R+P}-\Gamma_{AP}\Phi^2_{B+A}\Phi^2_{P+R}-\Phi^2_{A+B}\Phi^2_{R+P}/\Gamma_{AP}$
II	$4\Phi^2_{2A}+\Phi^2_{P+R}+\Phi^2_{R+P}$	$4\Phi^4_{2A}+\Phi^2_{P+R}\Phi^2_{R+P}-\Gamma_{AP}\Phi^2_{2A}\Phi^2_{P+R}-4\Phi^2_{2A}\Phi^2_{R+P}/\Gamma_{AP}$
III	$4\Phi^2_{2A} + 4\Phi^2_{2P}$	$4\Phi^4_{2A}+4\Phi^4_{2P} - 4\Phi^2_{2A}\Phi^2_{2P}(\Gamma_{AP}+1/\Gamma_{AP})$
IV	$\Phi^2_{A+B} + \Phi^2_{B+A} +\Phi^2_{P}$	$\Phi^2_{A+B}\Phi^2_{B+A} - \Phi^2_{A+B}\Phi^2_{P}/\Gamma_{AP}$
V	$4\Phi^2_{2A} + \Phi^2_{P}$	$4\Phi^4_{2A} - 4\Phi^2_{2A}\Phi^2_{P}/\Gamma_{AP}$
VI	$\Phi^2_{A+B}+\Phi^2_{B+A}$	$\Phi^2_{A+B}\Phi^2_{B+A}$
VII	$4\Phi^2_{2A}$	$4\Phi^4_{2A}$

reversible reaction, $\Phi_{1st}^2 = \Phi_A^2 + \Phi_P^2$ given in Satterfield (1970) and in eq. (1.28). A Thiele modulus symbol has been chosen for Φ_{1st} because of the direct relationship with irreversible reaction Thiele moduli in eq. (2.44), as well as because it multiplies the first-power concentration term. It also has a similar influence on calculated solutions as that of the Thiele modulus in first-order problems when higher order effects are minor. The first-order modulus, Φ_{1st}^2, is also independent of the scaling choice of eqs. (2.19) or (2.38). A general derivation for the four species reaction, $\nu_A A + \nu_B B \rightleftarrows \nu_P P + \nu_R R$, and $r_p = k_r \hat{c}_P \hat{c}_R - k_f \hat{c}_A \hat{c}_B$, gives the following expression for Φ_{1st}^2

$$\Phi_{1st}^2 = \frac{\nu_P L^2 k_r \hat{c}_{Ps}}{D_R} + \frac{\nu_R L^2 k_r \hat{c}_{Rs}}{D_P} - \frac{\nu_A L^2 k_f \hat{c}_{As}}{D_B} - \frac{\nu_B L^2 k_f \hat{c}_{Bs}}{D_A} . \qquad 2.45$$

Simple rules apply for deriving the expressions in Table 2.5 from eq. (2.45) when, for example, A and B are identical species, or when the reverse reaction is first-order (no R). Since complete expansions are given in Table 2.5, discussions of these rules are deferred until Chapter Three and the more complicated expressions for third-order kinetics.

The second dimensionless parameter, $6a_{1i}(6a_{1i} + 6a_{2i} + 2a_{3i})$ or Ψ, has no first-order analog, and in eq. (2.40) it is the coefficient of c''^2. Symbolic expansions for Ψ are given in Table 2.5. There it is seen to be composed of irreversible reaction Thiele moduli as Φ_{1st} plus the bridging parameter, Γ_{AP}. The irreversible reaction Thiele moduli appear only as products with themselves or other moduli. For the general second-order

problem just discussed above, Ψ can be expressed in terms of original physical constants as

$$\Psi = L^4 \left(\frac{v_P v_R k_r}{D_P D_R} - \frac{v_A v_B k_f}{D_A D_B} \right) (k_r \hat{c}_{Ps} \hat{c}_{Rs} - k_f \hat{c}_{As} \hat{c}_{Bs}) \; . \qquad 2.46$$

It is seen that Ψ is composed of a difference times the reaction rate at the slab surface. Both parts of this expression are of arbitrary sign, so Ψ can be either positive or negative. In fact Ψ could be zero for nonzero surface reaction rates through the first term in eq. (2.46). This leads to precise first-order behavior of the solution as will be discussed later in this chapter. Note that for irreversible reactions, k_r or k_f is zero, and Ψ is always positive. The parameter, Ψ, will be referred to as the second-order modulus. It is dimensionally similar to the fourth power of a Thiele modulus, $L^4 k^2 \hat{c}_{is}^2 / D^2$. The second-order modulus, Ψ, is independent of the chemical species selected as a derivational basis as was the case for Φ_{1st}^2 and unlike the case for the numerous a_{ij}. A discussion of simple rules to use eq. (2.46) to form the expressions in Table 2.5 will be deferred to Chapter Three as mentioned above.

The feasible ranges for Φ_{1st} and Ψ define a region somewhat smaller than a semi-infinite plane, $(\Phi_{1st} \geq 0, \Psi)$. Although Ψ can be positive or negative, its positive range is limited physically by the condition that all species' concentrations, $\hat{c}_i(x)$, must be real if the diffusion modified reaction expression (right-hand side of the diffusion equation) is set equal to zero. The dimensional, diffusion modified "equilibrium" concentrations are related to the dimensionless diffusion modified equilibrium concentration, $c''_{eq}(z)$, which constrains $c''(z)$ by

$$0 \le c''(z) \le c''_{eq}(z) = \frac{-\Phi_{1st}^2 + \sqrt{\Phi_{1st}^4 - 4\Psi}}{-2\Psi} \qquad 2.47$$

where the right-hand side arises from applying the quadratic formula to the right-hand side of eq. (2.40). This diffusion and reaction driven concentration shift generally does not lead to an equilibrium state if applied to the set of external surface concentrations in the absence of diffusional effects. In other words the extent of reaction of the diffusion modified rate expression is a physically different concept from that in homogeneous kinetics. Applying the requirement of real valued concentrations at equilibrium leads to the following physical parameter constraint

$$\Psi \le \frac{\Phi_{1st}^4}{4} \qquad 2.48$$

which ensures $c''_{eq}(z)$ is real and also implies $g_2 \ge 0$. The same result, i.e. that $\Phi_{1st}^4/4$ is the largest value available to Ψ, is also obtained by solving the problem: maximize $\Psi(\Phi_{A+B}^2, \Phi_{B+A}^2, \Phi_{P+R}^2, \Phi_{R+P}^2, \Gamma_{AP})$, subject to constant Φ_{1st}^2, and the species' parameters constrained to be positive.

An additional word is in order about the constraint in eq. (2.48). The equality in eq. (2.48) can be examined by expanding $\Phi_{1st}^4/4 - \Psi$ for Case I of Table 2.1 in the physical constants of the original problem to give

$$\Phi_{1st}^4 - 4\Psi = L^4 \left[k_f \left(\frac{\hat{c}_{As}}{D_B} - \frac{\hat{c}_{Bs}}{D_A} \right) + k_r \left(\frac{\hat{c}_{Ps}}{D_R} - \frac{\hat{c}_{Rs}}{D_P} \right) \right]^2 +$$

$$L^4 k_f k_r \frac{(D_A \hat{c}_{As} + D_P \hat{c}_{Ps})(D_B \hat{c}_{Bs} + D_R \hat{c}_{Rs})}{D_A D_B D_P D_R} \geq 0 \qquad 2.49$$

If species A and B are identical and $k_r = 0$, or if $\hat{c}_{As}/D_B = \hat{c}_{Bs}/D_A$ and $k_r = 0$, then $\Phi_{1st}^4/4$ - $\Psi = 0$. Similar conditions occur if the roles of (A, B, k_r) are switched with (P, R, k_f). Therefore the equality of eq. (2.48) always holds for the case of the irreversible reaction, 2A → products, and can occur in the case of the irreversible reaction A + B → products. The equality is not expected to ever occur for reversible reactions. This reflects the fact that even if products are not present at the surface, they will be present in the slab and will influence the achievable reaction rates in the slab.

The slab midplane concentration, either c'(0) or c''(0), must be obtained by solving a nonlinear equation to complete the analytical solution of eqs. (2.37) or (2.41). The development so far is such that c''(0) has a much narrower range than c'(0), which ranges from +∞ to -∞ in the (Φ_{1st}, Ψ) parameter space. The sign of c'(0) changes with the sign of Ψ, and when $|\Psi|$ is large, $|c'(0)|$ is also large. The rescaling to c'' in eq. (2.38) yielded some surprising results as seen in Figure 2.1, where only feasible combinations of Φ_{1st} and Ψ were used per eq. (2.48). Not only was c''(0) always positive, as expected, but it was seemingly bounded above by one-half. Integration of eq. (2.40) assuming the right-hand side is a constant equal to -1 gives one-half as the midplane concentration. If the magnitude of the dimensionless reaction rate decreases
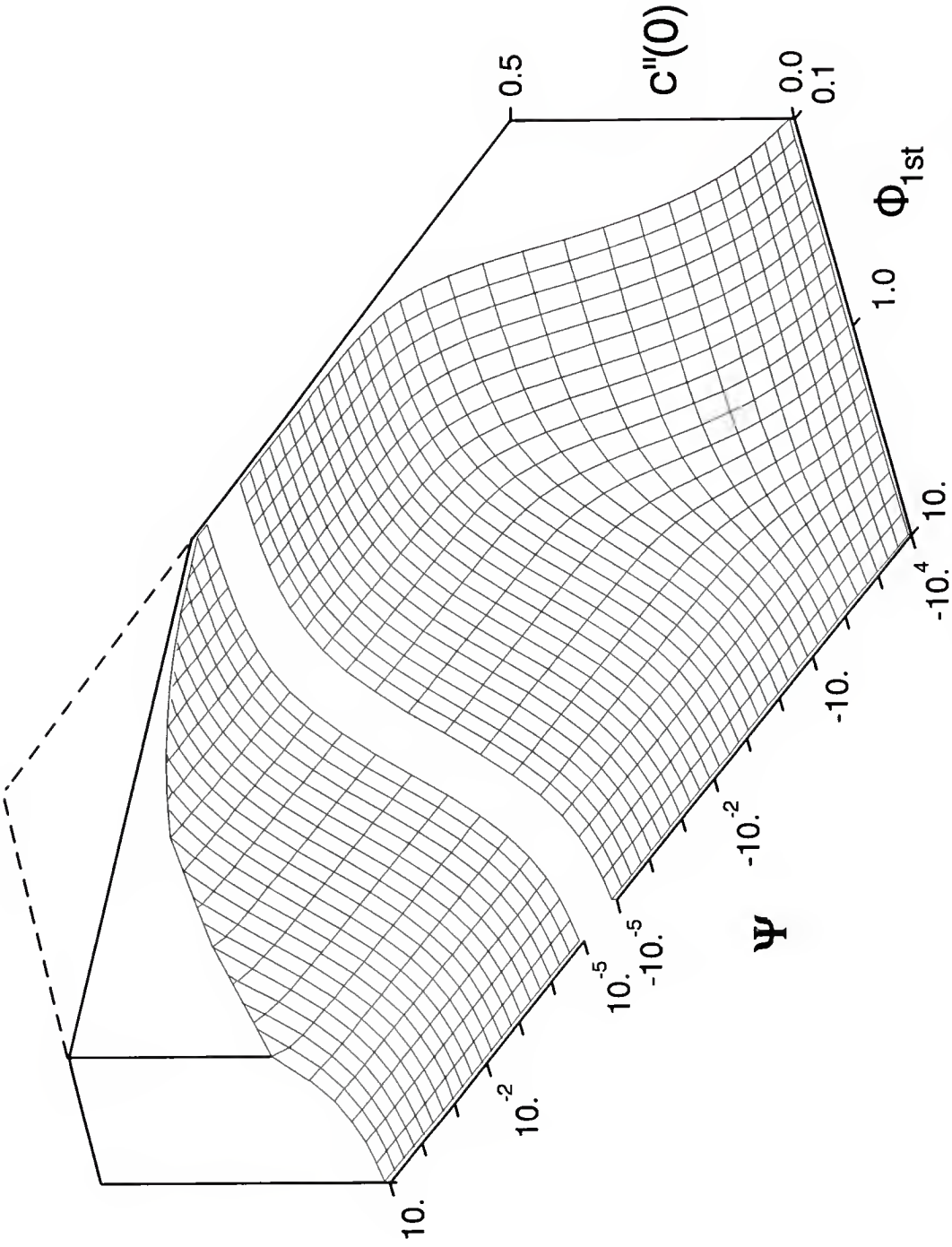
Figure 2.1 Plot of the dimensionless midplane concentration, c''(0), vs. the system parameters, Φ_{1st} and Ψ. Values of c''(0) are nearly equal between $\Psi = \pm 10^{-5}$.
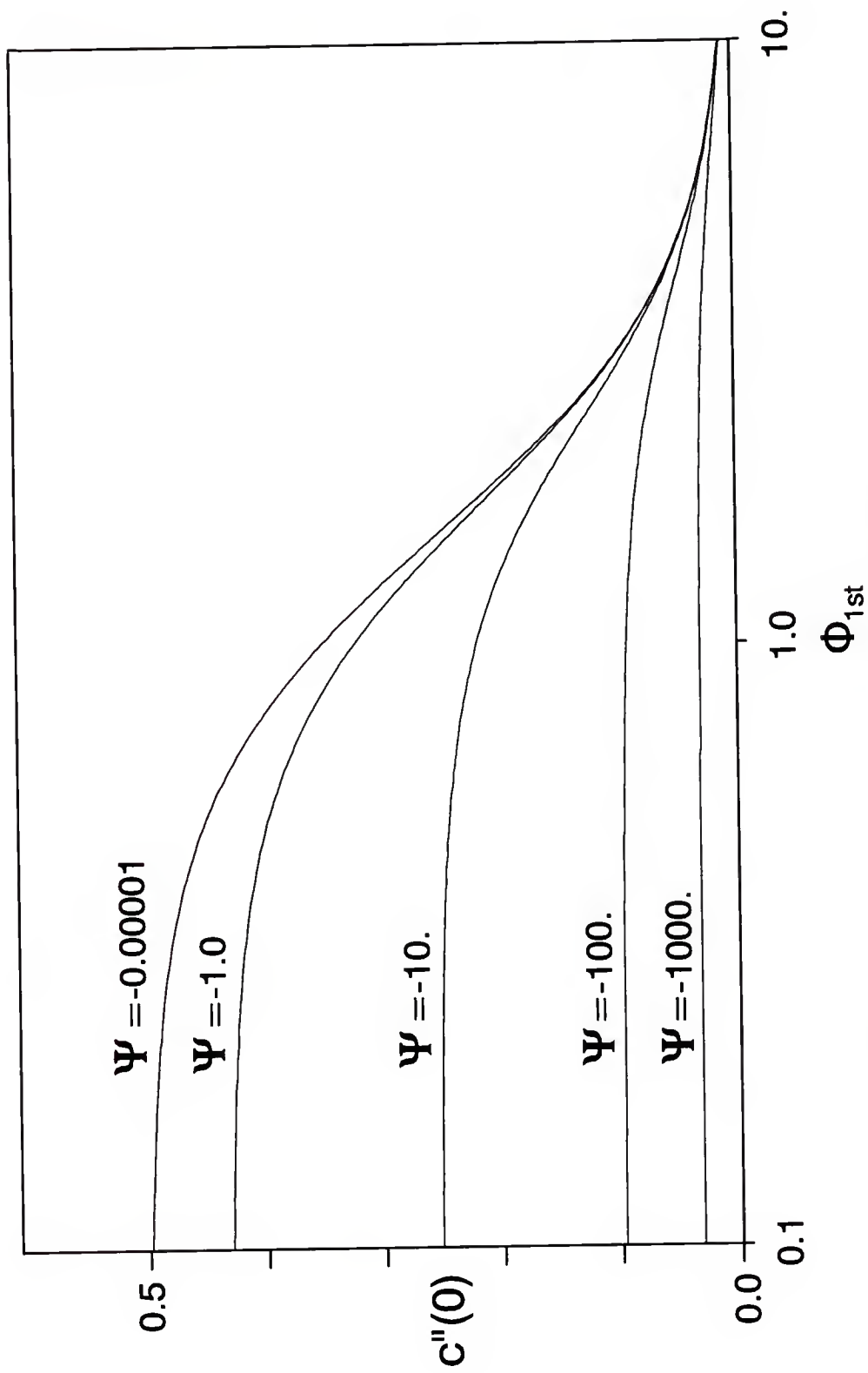
Figure 2.2 Semi-log plot of c''(0) vs. Φ_{1st} for some representative values of $\Psi < 0$.
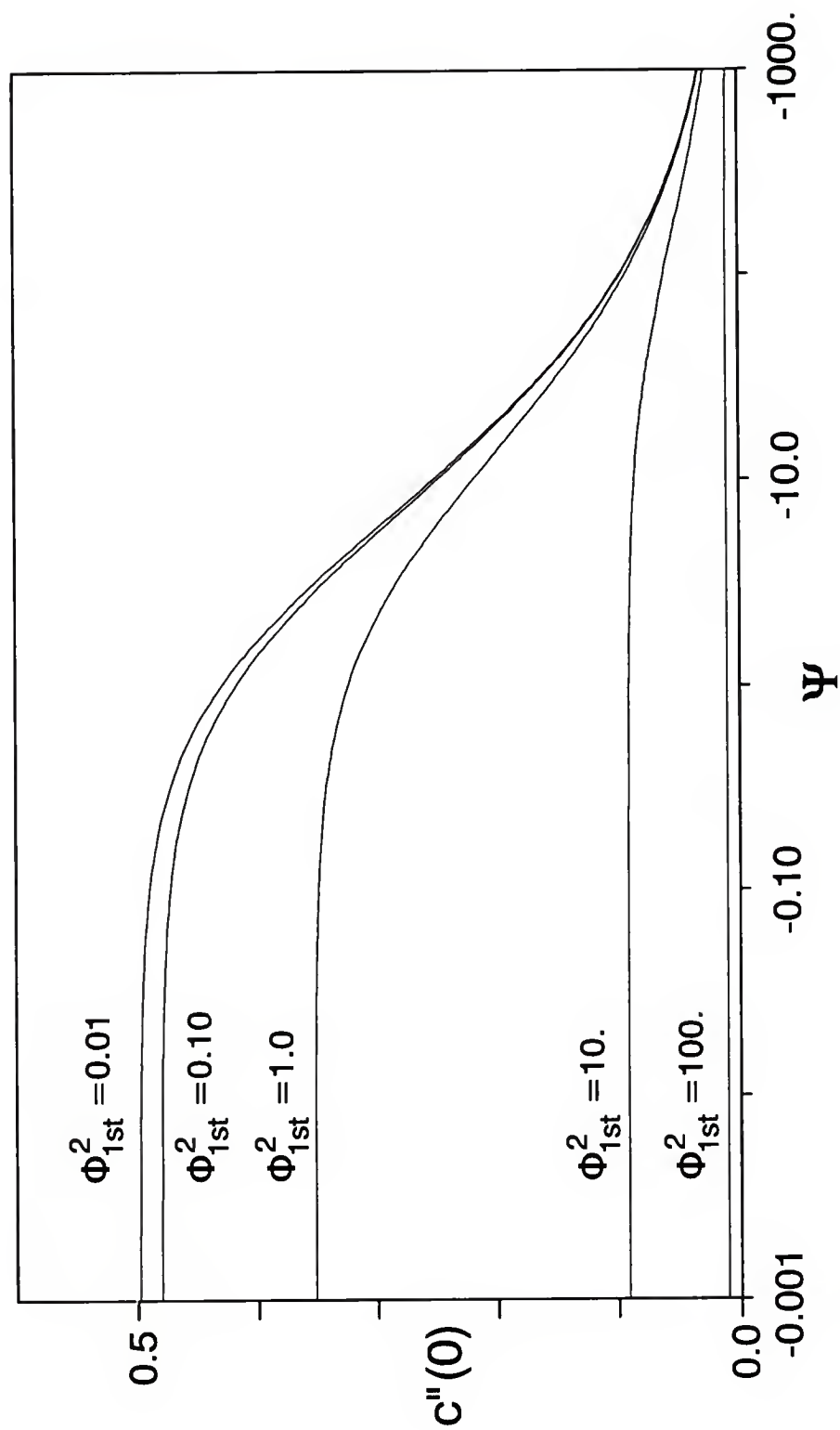
Figure 2.3 Semi-log plot of $c''(0)$ for some representative values of Φ^2_{1st}.

in the slab, the midplane concentration falls below one-half. Figures 2.2 and 2.3 provide some two-dimensional perspective on the surface of Figure 2.1 for selected parameter values. The limit of $\Phi_{1st} \to 0$ at constant Ψ gives values of $c''(0)$ that are within 0.5% of those shown for $\Phi_{1st}^2 = 0.01$. This limit has more relevance in less conventional kinetic schemes.

Figure 2.1 is somewhat deceptive. Since the surface concentration, $c''(1)$, equals zero, the maximum difference between $c''(1)$ and $c''(0)$ occurs at parameter ranges that correspond to high internal effectiveness factors. This is counter-intuitive in the sense that small concentration differences from surface to center are normally associated with diffusion free cases and large concentration differences are normally associated with diffusion limited cases. This phenomenon has to do with the inverse Ψ scaling constant in the definition of c''.

Eq. (2.47) had given one upper bound for $c''(0)$, $c''_{eq}(z=0)$, but it is only closely approached when $c''(0)$ goes to zero. For example, at $(\Phi_{1st}, \Psi) = (0.1, -10^{-5})$, $c''_{eq}(0) = 91.6$, implying $0 \leq c''(0) \leq 91.6$, which is a much broader range than zero to one half. Figure 2.4 plots the scaled departure of either $c'(0)$ or $c''(0)$ from the diffusion modified equilibrium conversion as given in eq. (2.47) and where

$$c'_{eq}(z) \equiv \frac{-\Phi_{1st}^2 + \sqrt{\Phi_{1st}^4 - 4\Psi}}{2} \qquad 2.50$$

for c'_{eq}. Note that $(c'_{eq} - c'(0))/c'_{eq} = (c''_{eq} - c''(0))/c''_{eq}$. The departure from equilibrium conversion is negligible for strongly diffusion-limited cases. It is not

formally proper to discuss the solution of eq. (2.40) at $\Psi = 0$, since the equation was derived using division by Ψ. The solution to eq. (2.21) for c', however, passes through c'(0) = 0 at $\Psi = 0$, changing sign in the process, i.e. c'' approaches zero over zero as $\Psi \to 0$.

Figure 2.4 further substantiates one of the claims made earlier on the behavior of the slab midplane concentration. The surface shown characterizes the approach to either diffusion modified equilibrium conversion (for reversible reactions), or complete conversion (for irreversible reactions), at the slab midplane. This approach is quite strong as $\Psi \to -\infty$ and/or $\Phi_{1st} \to \infty$. When $\Psi \to \Phi_{1st}^4/4$ ($g_2 = 0$) as $\Phi_{1st} \to \infty$; however, the approach to high midplane conversions appears to be retarded, i.e. along the diagonal boundary of the parameter space. The accuracy of eq. (2.54), below, for $\hat{c}_i(0)$ is also qualitatively indicated in Figure 2.4.

If one defines

$$c''_o \equiv \lim_{\Psi \to 0}(c''(0)) = \frac{1 - 1/\cosh(\Phi_{1st})}{\Phi_{1st}^2} \qquad 2.51$$

then the solution of eq. (2.41) for c''(0) should match that of the first-order problem, see Chapter One, for

$$\frac{d^2 c''}{dz^2} = \Phi_{1st}^2 c'' - 1 \qquad 2.52$$

given by c''_o above. The group, $(c''_o - c''(0))/c''_o$, represents a scaled measure of the departure of the dimensionless midplane concentration for second-order reactions from
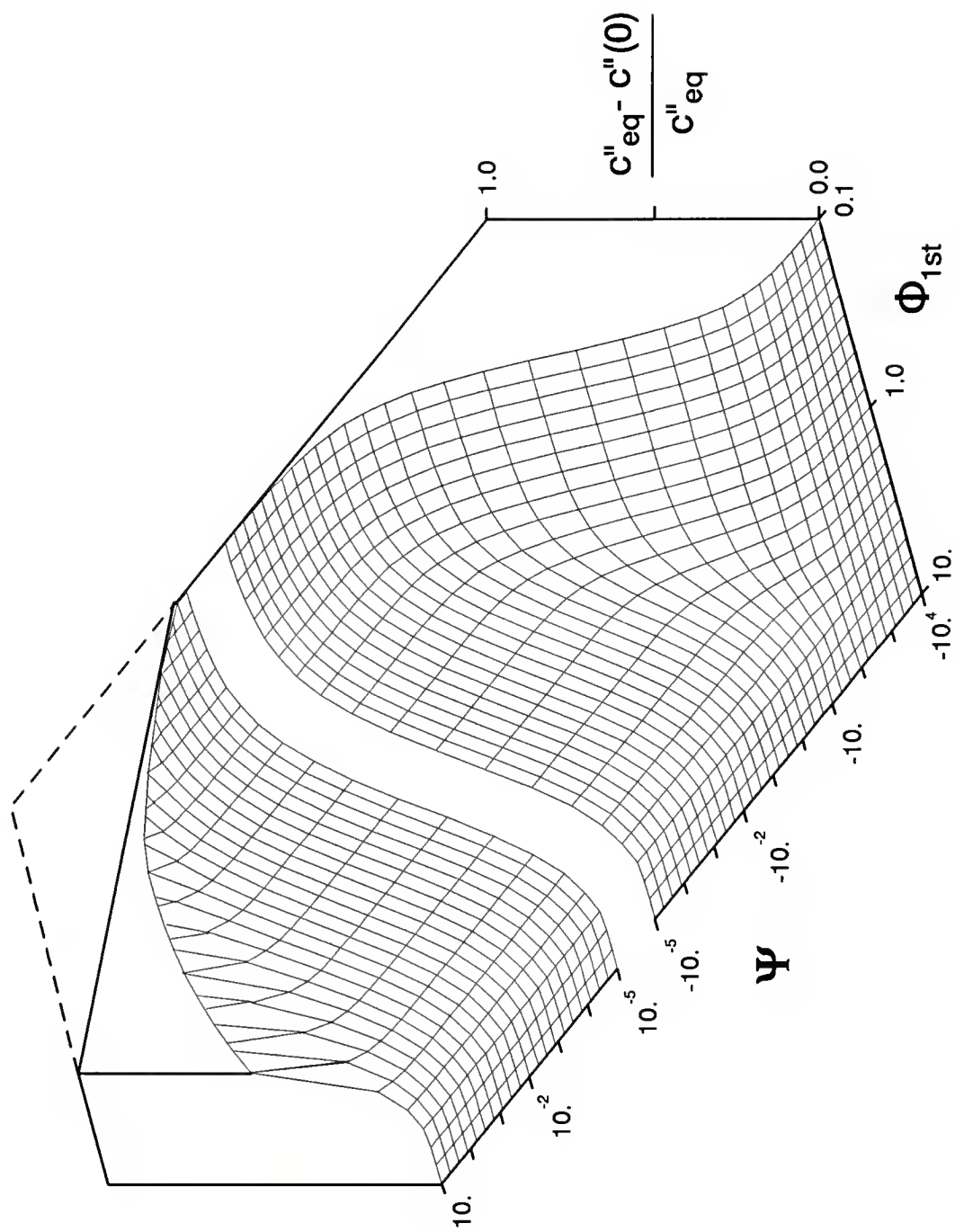
Figure 2.4 The scaled departure of the dimensionless midplane concentration from the equilibrium state of the reaction-diffusion equation.

that of the first-order problem. This group is plotted in Figure 2.5 against Φ_{1st} and Ψ. The plot includes contours showing the demarcation between values within 1% of first-order behavior and beyond. Figures 2.4 and 2.5 are somewhat complimentary in their regions of small departure. Eq. (2.52) gives c''(0) as a function of Φ_{1st} at $\Psi = \pm 10^{-5}$ to within 0.1%. The double limit $|\Psi| \rightarrow 0$, $|\Phi_{1st}| \rightarrow 0$ gives c''(0) = 0.50 exactly. Numerically, c''(0) < 0.5 at all 1092 values of Φ_{1st} and Ψ examined.

Combining eqs. (2.19) and (2.51) gives an approximate relationship between the dimensionless species' concentration, $\hat{c}_i(0)$ and a_{1i}, Φ_{1st} and Ψ

$$\hat{c}_i(0) \approx \hat{c}_{is}\left(1 - \frac{\Psi(1 - 1/\cosh(\Phi_{1st}))}{6a_{1i}\Phi_{1st}^2}\right) \qquad 2.53$$

approximately valid for $|\Psi| \leq 0.1$ by derivation, but applicable at some larger $|\Psi|$ when Φ_{1st} is also large per the limits in Figure 2.5. Alternatively, when (c''$_{eq}$ - c''(0))/c''$_{eq}$ in Figure 2.4 is small, c''(0) is well approximated by eq. (2.51). This leads to a second approximate expression for $\hat{c}_i(0)$

$$\hat{c}_i(0) \approx \hat{c}_{is}\left(1 + \frac{-\Phi_{1st}^2 + \sqrt{\Phi_{1st}^4 - 4\Psi}}{12 a_{1i}}\right) \qquad 2.54$$

which is acceptable for $\Phi_{1st} > 5$ or $\Psi < -1000$. Eqs. (2.53) and (2.54) together cover much of the parameter space. Therefore, if one does not wish to work with the analytical solution, then eqs. (2.53) and (2.54) offer one alternative method for estimating the midplane concentration and ultimately the internal effectiveness factor.
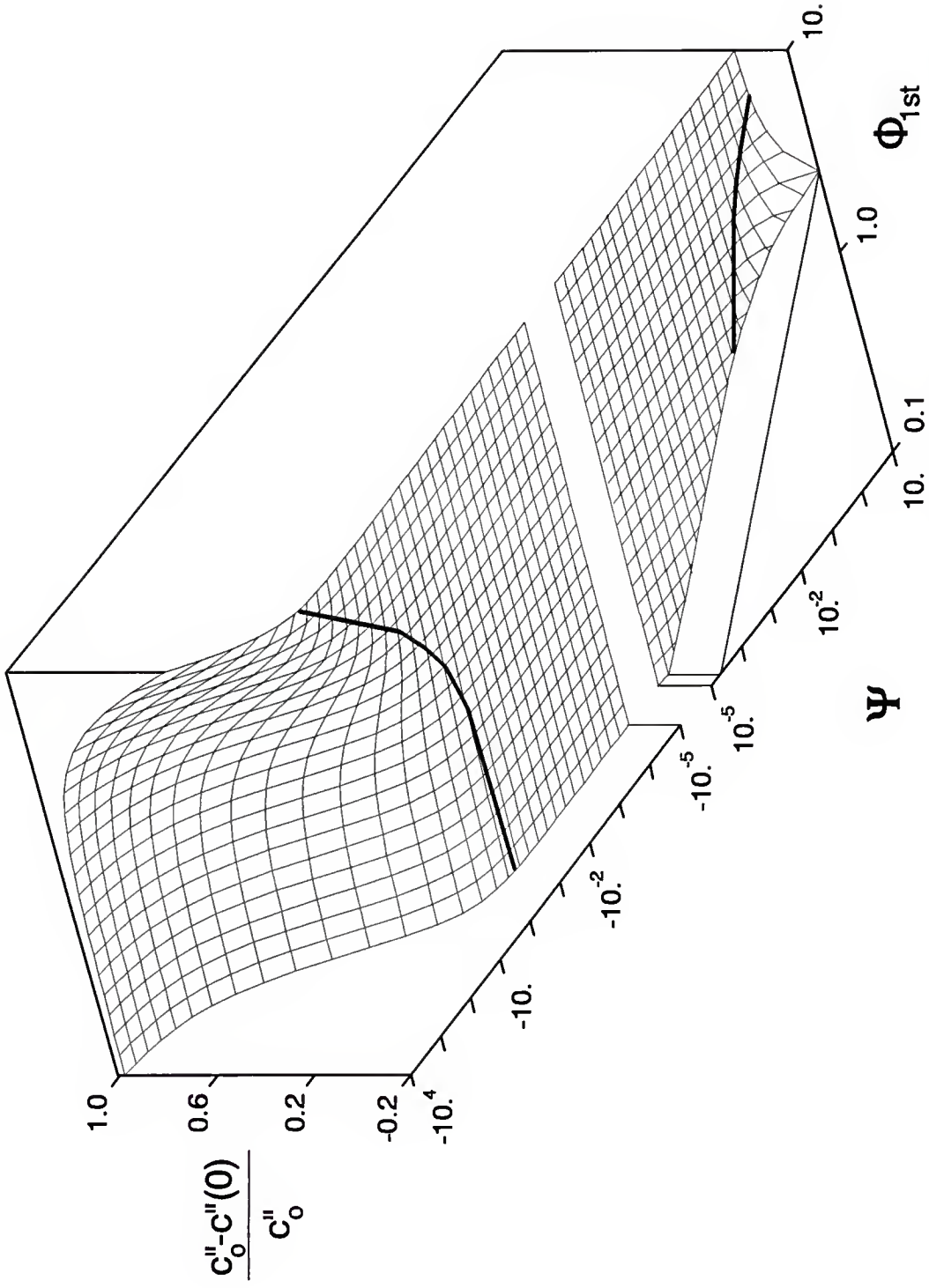
Figure 2.5 The scaled departure of the dimensionless midplane concentration from first-order behavior. Bold lines are contours at fractional deviations of ± 0.01.

Finally, one should not generally think in terms of Φ_{1st} going to zero at constant Ψ. This can be seen by noting in Table 2.5 that when $\Psi < 0$, $|\Psi| \leq M\Phi_{1st}^4$, where M is a constant, such as $\Gamma_{AP}/2$ for Case I (when $\Gamma_{AP} \geq 1$). In other words, the magnitude of Ψ is generally constrained by the magnitude of Φ_{1st}^2 and can not be chosen independently in most actual physical systems; however, there are possibilities for exceptions. The point is fairly subtle. How can Ψ go to zero much more slowly than Φ_{1st}^2? First note that Φ_{1st} goes to zero if (1) $L \rightarrow 0$, (2) $k_f \rightarrow 0$ and $k_r \rightarrow 0$, (3) $D_i \rightarrow \infty$ for all species, or (4) $\hat{c}_{As}/D_B \rightarrow 0$, $\hat{c}_{Bs}/D_A \rightarrow 0$, $\hat{c}_{Ps}/D_R \rightarrow 0$, and $\hat{c}_{Rs}/D_P \rightarrow 0$. Then note that Ψ goes to zero under the first three limits above, but the fourth must be modified to (4')
$\hat{c}_{As}\hat{c}_{Bs}/D_A D_B \rightarrow 0$, $\hat{c}_{Ps}\hat{c}_{Rs}/D_P D_R \rightarrow 0$, $\hat{c}_{As}\hat{c}_{Bs}/D_P D_R \rightarrow 0$, and $\hat{c}_{Ps}\hat{c}_{Rs}/D_A D_B \rightarrow 0$. Since only the first half of condition (4') is forced by condition (4) for Φ_{1st}, it is still possible for $|\Psi|$ to remain large, but the rest of condition (4') often follows from condition (4) in practice. Still the key terms are $\hat{c}_{As}\hat{c}_{Bs}/D_P D_R$ and $\hat{c}_{Ps}\hat{c}_{Rs}/D_A D_B$. Consequently, only under unusual circumstances will $|\Psi|$ be large when Φ_{1st} is small.

The Weierstrass Pe-Function, $\wp$

The Weierstrass elliptic Pe-function, $\wp$, is discussed in Whittaker and Watson (1950) and other texts. One of its original uses was in the study of dynamics of nonlinear pendulum motion, with friction dependent on displacement squared and/or cubed, and the sin(x) expansion increased to include the cubic as well as linear term. In this situation the Weierstrass elliptic function provided an analytical solution to an approximate physical model. Here, if the assumptions on diffusivity, etc. are valid, the

Weierstrass elliptic function is an analytical solution to a true physical system, since the reaction rate forcing function is not approximated. The Pe-function, $\wp$, is a doubly periodic function in the complex plane, i.e. $\wp(z + 2m\omega_1 + 2n\omega_2) = \wp(z)$ for any integers m,n. The ratio of ω_1/ω_2, the two half-periods, is not purely real, and the only singularities in the finite part of the plane are double poles at $z - 2m\omega_1 - 2n\omega_2 = 0$. The two periods, $2\omega_1$ and $2\omega_2$, define a single function. Many equivalent period pairs can define the same function; however, all such pairs are linked by common invariants, g_2 and g_3. Abramowitz and Stegun (1964) give a procedure for determining a base pair of frequencies from the two invariants, but this is not germane to the present problem. They also give an expression for $\wp$ in terms of the two invariants, g_2 and g_3,

$$\wp(z; g_2, g_3) = \frac{1}{z^2} + \sum_{k=2}^{\infty} C_k z^{2k-2} \qquad \qquad 2.55$$

where there is no constant term, and

$$C_2 = \frac{g_2}{20} \qquad \qquad C_3 = \frac{g_3}{28} \, . \qquad \qquad 2.56$$

$$C_k = \frac{3 \sum_{m=2}^{k-2} C_m C_{k-m}}{(2k+1)(k-3)} \qquad k \geq 4 \qquad \qquad 2.57$$

Eq. (2.55) is the definition of choice for evaluating the Pe-function in this work. Abramowitz and Stegun (1964) give the coefficients up to C_{19} in terms of C_2 and C_3 only. If $g_2 = 20$ and $g_3 = 28$, then $C_{19} = 6.04*10^{-6}$. (Evaluation of any midplane

Table 2.6 Typical Values of the Weierstrass Pe-Function

Invariants		$\wp(1;g_2,g_3)$	First Five Terms of $\wp$	Error (%)
g_2	g_3			
0.0	1.0	1.035813	1.035714	0.01
0.0	3.0	1.108031	1.107143	0.08
1.0	1.0	1.087146	1.087035	0.01
1.0	-1.0	1.014733	1.014632	0.01
-1.0	1.0	0.986156	0.986061	0.01
-1.0	-1.0	0.915691	0.915606	0.01
0.1	0.1	1.008586	1.098585	0.0001
-0.1	-0.1	0.991443	0.991442	0.0001
3.0	-3.0	1.046923	1.045974	0.091
5.0	2.0	1.3487	1.3471	0.116
5.0	-2.0	1.1955	1.1945	0.081
20.0	28.0	3.856	3.606	6.48
20.0	-28.0	1.180	1.061	10.12
40.0	-20.0	3.423	3.229	5.65

concentration from the final boundary condition requires summing the series at $z = 1$.) Some representative values of $\wp(1;g_2,g_3)$ are given in Table 2.6. This summation will be time consuming, except for a digital computer, if g_2 and/or g_3 are large in magnitude. Note, however, that if $(g_2 g_3) < 0$ and $|g_2/g_3| \approx O(1)$, then $\wp(1;g_2,g_3)$ and $\wp(1;-g_2,-g_3)$ are closer to one than $\wp(1;g_2,-g_3)$ and $\wp(1;-g_2,g_3)$. In many regions of engineering interest $g_2 > 0$ and $g_3 < 0$. Convergence of the series for $0 < z \leq 0.8$ can be quite rapid, regardless of the invariant magnitudes, because powers of z tend to dominate over products of the invariants.

The two invariants, g_2 and g_3, are approximately of the same order of magnitude as the largest irreversible reaction Thiele modulus, e.g. Φ_{A+B}^2, raised to the power of two or three respectively. Consequently, when the individual irreversible reaction Thiele moduli get near four, g_2 can easily be greater than 20. (An exception is Case VII kinetics, where g_2 is identically 0). The other invariant, g_3, is frequently smaller in magnitude than g_2 for weakly to moderately diffusion limited reversible reactions, and tends to be negative for the conventional second-order reactions considered here. When one or more irreversible reaction Thiele moduli for a problem is near three, either g_2 and/or g_3 could be larger than twenty in magnitude and convergence of $\wp$ will take more than just a few terms. It is best to determine a few of the coefficients in eq. (2.55) before assessing the unwieldiness of the exact solution. Larger invariant magnitudes were found to be indicative of steeper concentration gradients and stronger diffusional limitations. The practical point being made is that for small invariant magnitudes, $\wp$ is

easily handled with a pocket calculator. A computer evaluation of a lengthy truncated series is only required for larger invariant magnitudes.

The dependence of $\wp$ on $c''(0)$ can be very weak for second-order reversible reactions, since g_3 is proportional to powers of the two fundamental parameters added to similar terms multiplied times $c''(0)$, which is always bounded by one-half for the reactions being discussed in this chapter. Furthermore, $|g_3|$ tends to be a maximum at the equilibrium conversion, i.e. a root of $-\Psi c''^2 + \Phi_{1st}^2 c'' - 1$ or $c'^2 + \Phi_{1st}^2 c' + \Psi$. For fixed $\wp(1; g_2, \hat{g}_3)$, where $\hat{g}_3$ is an estimate of the true g_3, eq. (2.41) becomes a simple quadratic equation for $c''(0)^2$

$$4\Psi c''(0)^2 - (5\Phi_{1st}^2 + 12\wp(1; g_2, \hat{g}_3))c''(0) + 6 = 0. \qquad 2.58$$

The situation above is simpler for the two irreversible second-order reactions, Cases VI and VII, but not better. These reactions should have only two or one modulus respectively for even cruder analyses. For Table 2.1, Case VI, $(A + B \rightarrow)$, the two fundamental parameters depend on only two species' parameters, Φ_{A+B}^2 and Φ_{B+A}^2, as do the invariants

$$g_2 = \frac{\Phi_{B+A}^2 - \Phi_{A+B}^2}{12} \qquad 2.59$$

$$g_3 = \frac{(\Phi_{A+B}^2 - \Phi_{B+A}^2)^3}{216} + \left(\frac{\Phi_{A+B}^2}{6}\right)^3 \left(\frac{2\Phi_{A+B}^2 c_A^3(0)}{3} + (\Phi_{B+A}^2 - \Phi_{A+B}^2)c_A^2(0)\right) \qquad 2.60$$

since $c_A(0)$ is also a function of Φ^2_{A+B} and Φ^2_{B+A}. Barring a major difference in diffusivities of A and B, or a large departure from a stoichiometric surface concentration, g_2 and g_3 will be manageable numbers up to quite large Φ^2. For Table 2.1, Case VII, (2A $\rightarrow$ products), there should be only a single parameter, and Φ^2_{1st} and Ψ are directly related as expected. The first invariant, g_2 is identically zero and

$$g_3 = \frac{4\,\Phi^6_{2A}c^3_A(0)}{27} \qquad\qquad 2.61$$

When $g_2 = 0$, only every third term in the expansion of $\wp$ is nonzero. Nevertheless, in both Cases VI and VII there is a limiting computational aspect at large values of the irreversible reaction Thiele moduli.

This situation is closely related to one degeneracy or simplification of the Pe-function that occurs when the discriminant of the canonical polynomial, $4\sigma^3 - g_2\sigma - g_3$, is zero, i.e. $g^3_2 - 27g^2_3 = 0$. This is the traditional criterion for a cubic polynomial to have a repeated root adapted to the canonical form used with the Weierstrass elliptic function. The discriminant of the canonical polynomial characterizes its roots. When the discriminant is positive there are three real roots, and when it is negative there is only one. It is easiest to use the c' equations for further analysis of zero valued discriminants

$$g_3 = \pm\sqrt{\frac{g^3_2}{27}} \qquad\qquad 2.62$$

which can be expanded to

$$4c'(0)^3 + 6\Phi_{1st}^2 c'(0)^2 + 12\Psi c'(0) + 6\Phi_{1st}^2 \Psi - \Phi_{1st}^6 = \pm(\Phi_{1st}^4 - 4\Psi)^{1.5} \quad 2.63$$

This expression can be treated as two cubic equations in c'(0). All six roots have been found and are given by

$$c'(0) = \frac{-\Phi_{1st}^2 \pm \sqrt{\Phi_{1st}^4 - 4\Psi}}{2} \qquad\qquad 2.64$$

$$c'(0) = \frac{-\Phi_{1st}^2 \pm 2\sqrt{\Phi_{1st}^4 - 4\Psi}}{2} \qquad\qquad 2.65$$

where the two roots given by eq. (2.64) are both double roots of eq. (2.63) in addition to also being the roots of the diffusion modified reaction equilibrium expression, eq. (2.50). Thus the discriminant equality is expected to be met asymptotically in the limit as the midplane concentration approaches the diffusion modified reaction equilibrium concentration. The negative root in eq. (2.66) gives a concentration further from the surface concentration than the negative root in eq. (2.65), and is physically unachievable. It is potentially possible that the surface given by the positive root of eq. (2.66) intersects the c'(0) of (Φ_{1st}^2, Ψ) diffusion reaction solution surface, eq. (2.37). This case was left unexplored, but methods were developed to deal with zero or near zero discriminants in general in the computer codes used to generate general solution surfaces.

For Table 2.1, Case VII, $c_A(0)$ goes to 0 as Φ_{2A}^2 goes to infinity, and g_3 goes to zero, so both g_2 and g_3 are zero, and again the discriminant approaches zero. When

there is a repeated root, eqs. (2.18), (2.21) and (2.40) can be integrated using conventional methods to give concentration profiles as functions of either $\sin^2(z)$ or $\sinh^2(z)$ depending on the sign of the repeated root; see below.

One special case in the analysis of the discriminaant occurs when $c'(0) = c'_{eq} = c'_s = 0$, i.e. a gradient free case, and therefore the second derivative is zero. This leads to a line in the (Φ^2_{1st}, Ψ) parameter space, $\Psi = 0$. Crossing this line in parameter space corresponds to changing the number of real roots of the canonical polynomial. On this line, the numerator of eq. (2.37) for $c'(z)$ is zero, and no solutions are obtained for which $c'(0) \neq 0$. If the discriminant of the canonical cubic polynomial is zero, and a double root, $\hat{r}_1$, exists, then the third root, $\hat{r}_3$, is equal to $-2\hat{r}_1$; see Abramowitz and Stegun (1964). For a positive double real root, $\hat{r}_1$, $\wp$ is given by

$$\wp(z; g_2, g_3) = \hat{r}_1 + \frac{3\hat{r}_1}{\sinh^2(\sqrt{3\hat{r}_1}\, z)} \qquad \hat{r}_1 > 0 \qquad\qquad 2.66$$

Since $\sinh^2(x) = (\cosh(2x) - 1)/2$, this gives approximately a first-order concentration profile expression when sutstituted into either eq. (2.37) or (2.41). The result is that the dimensionless concentration depends on the inverse of an inverse of a hyperbolic cosine function plus supporting constants. Two other cases arise

$$\wp(z; g_2, g_3) = \hat{r}_1 - \frac{3\hat{r}_1}{\sin^2(\sqrt{-3\hat{r}_1}\, z)} \qquad \hat{r}_1 < 0 \qquad\qquad 2.67$$

or

$$\wp(z; g_2, g_3) = \frac{1}{z^2} \qquad \hat{r}_1 = 0 . \qquad\qquad 2.68$$

The last equation is for a triple root, which only occurs when all three roots are equal to zero. These equations give a little more insight into the nature of Weierstrass Pe-function. The physical significance of the double root cases to the nature of the Pe-function is that one of the two characteristic periods of $\wp$ becomes infinite. The Pe-function then becomes simply periodic. The periodicity of the double poles of the Weierstrass Pe-function then goes as the inverse of the square of the simple zeroes of $\sin(2\omega x)$ or $\sinh(2\omega iy)$, for $z = x + iy$.

If g_2 and g_3 are both real and if the discriminant is positive, then there are three distinct real roots, $\hat{r}_1 > \hat{r}_2 > \hat{r}_3$, and $\wp$ is related to Jacobi elliptic functions, e.g. sn(z), by relations such as

$$\wp(z; g_2, g_3) = \hat{r}_3 + \frac{\hat{r}_1 - \hat{r}_3}{sn^2(\sqrt{\hat{r}_1 - \hat{r}_3}\, z)} . \qquad\qquad 2.69$$

Other relations with other Jacobi elliptic functions apply for other root cases. Since no roots are known in advance due to their dependence on the unknown midplane concentration, these expressions are both awkward in applications and difficult to generalize much as was the case for Thiele and his elliptic integrals (1937). Eq. (2.37) with $\wp$ is preferred as being more general, since it holds throughout the parameter space regardless of the number of real roots.

Thus an analytical solution has been derived for the Dirichlet problem for one-dimensional Cartesian coordinates in terms of the Weierstrass elliptic Pe-function for all seven cases of Table 2.1, subject only to some practical computational limits as described above. This solution becomes the focal point for further analysis.

Concentration Profiles From the Analytical Solution

It was mentioned earlier that, if the two invariants both exceed 20, then the computational effort for determining $\wp$ becomes significant. Simplifications should occur in the other extreme of small invariant magnitudes. Consider the problem of determining $c'(0)$ using eq. (2.37). From eq. (2.56) the expansion of $\wp$ has the following form

$$\wp(z; g_2, g_3) = \frac{1}{z^2} + \frac{g_2 z^2}{20} + \frac{g_3 z^4}{28} + \frac{g_2^2 z^6}{1200} + \frac{3 g_2 g_3 z^8}{6160} + \dots \qquad 2.70$$

In the seven discussed cases, g_2 is *ab initio* known. Therefore the first, second, and fourth terms in $\wp$ are known functions of z, while the third and fifth terms are linear in the unknown invariant, g_3. Recall that

$$g_3 = \frac{4 c'(0)^3 + 6 \Phi_{1st}^2 c'(0)^2 + 12 \Psi c'(0) + 6 \Phi_{1st}^2 \Psi - \Phi_{1st}^6}{216}. \qquad 2.71$$

To find the maximum feasible range of g_3, set $dg_3/dc'(0)$ equal to zero, giving (after multiplying by 18)

$$c'(0)^2 + \Phi_{1st}^2 c'(0) + \Psi = 0 \qquad 2.72$$

which is nothing more than the dimensionless diffusion modified rate expression evaluated at the midplane concentration. So a maximum or minimum in g_3 occurs at the equilibrium concentration. Thus, c'(0), bounded by the surface concentration and equilibrium concentration, sets the possible range of g_3 for given parameters.

Table 2.6 indicates that a five term expansion has 99.9% accuracy at z = 1 when $|g_2| < 3$ and $|g_3| < 3$. The five term expansion for $\wp$ is linear in g_3, so eq. (2.37) is approximately a quartic equation for c'(0). Using just the first two terms of the expansion for $\wp$ is within about 10% for this condition (and gets progressively better for smaller invariants), but leads at once to an easily solvable quadratic equation for c'(0)

$$c'(0) = \frac{-5\,\Phi_{1st}^2 - 12 - 0.6g_2}{8} \pm$$
$$\frac{\sqrt{25\,\Phi_{1st}^4 + 120\,\Phi_{1st}^2 + 144 + (6\,\Phi_{1st}^2 + 14.4)g_2 + 0.36g_2^2 - 96\,\Psi}}{8}$$

2.73

where the positive sign must generally be chosen. This equation estimates c'(0) better than the two term expansion estimates $\wp$, and can itself be sufficiently accurate for small $|g_2|$ and $|g_3|$. A two-step method to estimate c'(0) is suggested for $|g_2|$, $|g_3| < 10$. Use the above quadratic equation to estimate c'(0), use the c'(0) obtained to estimate g_3, eq. (2.72), use the five term expansion to estimate $\wp$ and use eq. (2.37), which becomes quadratic with an estimate of $\wp$, to obtain a new solution for c'(0).

The following example illustrates the procedure. Given

$$\Phi_{1st}^2 = 15 \qquad \Psi = 27$$

2.74

calculate g_2 from eq. (2.34).

$$g_2 = 9.75 \qquad 2.75$$

Find the equilibrium concentration from eq. (2.73)

$$c'_{eq} = -2.09167 \qquad 2.76$$

For the first step, make a crude estimate of $\wp$ using

$$\wp \approx 1 + \frac{g_2}{20} = 1.49 \qquad 2.77$$

Find a first estimate of c'(0) from eq. (2.74) above.

$$c'(0) \approx -1.21 \qquad 2.78$$

Use c'(0) to estimate g_3.

$$\hat{g}_3 = -5.61165 \qquad 2.79$$

For the second step estimate $\wp$ with the five term expansion, eq. (2.71).

$$\hat{\wp}(1; g_2, \hat{g}_3) \approx 1.3397 \qquad 2.80$$

Recalculate c'(0) with eq. (2.59) at z=1 and the above $\wp$ giving

$$c'(0) \approx -1.945 . \qquad 2.81$$

Repeating the second step gives c'(0) = -1.948, while the exact solution is -1.946, so the above estimate is within one per cent. The magnitude of g_2 is approximately ten, so this is a borderline case of the method. The center concentration is at about 93% potential conversion relative to 100% at diffusion modified reaction equilibrium, so this example is not in the diffusion free region.

The two-step method is not limited to c'(0) but could be applied to c''(0) or $c_A(0)$. As the magnitudes of the two invariants get larger, the simple hand calculation above is less accurate. The two-step method for quick hand calculation is thus limited to the region of small to moderate diffusional effects, even though that may cover 90% of the possible range of c'(0) values, as in the above example. In the region of strong diffusional effects, a longer expansion of the Weierstrass Pe- function is required.

First-Order Subcases of the General Problem

For the cases described earlier, there are numerous subcases that exhibit pseudo-first-order or even true first-order kinetics. Maymo and Cunningham (1966) observed that for Table 2.1, Case VI, irreversible kinetics, as D_B goes to infinity, $\hat{c}_B$ goes to $\hat{c}_{Bs}$, and the rate becomes approximately equal to the pseudo-first-order form $(k_f\hat{c}_{Bs})\hat{c}_A$. Similar arguments, applied to one or more diffusivities, could be extended to any of Cases I-V.

Cases I-III in Table 2.1 all have another property in that at quite ordinary parameter values, all the coefficients of the c''^2 term, i.e. Ψ, vanish as do the a_{1i} in all of the species' governing ODE's. This arises from the left-hand difference in the equation for Ψ, eq. (2.46). This degenerate first-order behavior occurs not as a limiting behavior as in Case VI above, but in the middle of the parameter space. This phenomenon is independent of the initial coordinate geometry (slab, sphere, cylinder), and is not a statement of reaction equilibrium. This is a degenerate zero in the discriminant of the canonical cubic polynomial not clearly shown in the development

using c'(0). To explore this situation requires the initial dimensionless species

concentration equations in terms of the a_{ji}. Developing the discriminant in the a_{ji} for a

species, I, gives

$$g_2^3 - 27g_3^2 = a_1^2 [(36a_2^2 a_3^2 - 64a_1 a_3^3) + (108a_1 a_2 a_3 - 54a_2^3)a_4 - (27a_1^2)a_4^2] \quad 2.82$$

where

$$a_4 = -4a_1 c_i^3(0) - 6a_2 c_i^2(0) - 4a_3 c_i(0) . \quad\quad\quad 2.83$$

As seen from eq. (2.82), $a_{1i} = 0$ also corresponds to a case where the discriminant of

the canonical polynomial equals zero independent of the six c'(0) zeroes derived earlier.

A degeneracy in the definition of c' or c'' occurs when $a_{1i} = 0$. Thus all solutions in

the neighborhood of the plane $a_{1i} = 0$, or $\Psi = 0$, are strongly first-order in character.

This plane does not apparently correspond to any further unusual behavior of the solution

other than that numerically $(a_2)_i = (a_2)_j$, $(i,j = A,B,P,R)$ and $6a_{2i} = \Phi_{1st}^2$. Something of

the physical significance of $6a_{2i}$ is thus revealed. In the general second-order reversible

kinetics for Cases I-III, $6a_{2i}$ can be rewritten as

$$6a_{2i} = \Phi_{1st}^2 - 12a_{1i} . \quad\quad\quad 2.84$$

So for $a_{1i} \neq 0$, $6a_{1i}$ carries the species dependent deviation from first-order behavior for

the coefficients of both the first-order and second-order terms, c_i and c_i^2, in eq. (2.18).

The above relationship, eq. (2.84), holds for all species in all seven cases, although its

existence cannot be motivated by the above line of reasoning (search for first-order

behavior), especially for the two irreversible cases where some balance between reactant

and product Thiele moduli is impossible. The initial recognition of eq. (2.84) occurred

prior to the discovery of the two-parameter basis and was the first clue that more fundamental parameters might exist. When a_{1i}, or Ψ, is zero, it makes little sense to use c', defined with muliplication by a_{1i}, or c'', defined with division by Ψ. For Cases I-III, when $a_{1i} = 0$

$$\frac{d^2 c_i}{dz^2} = 6 a_{2i} c_i + 2 a_{3i} = \Phi_{1st}^2 c_i + 2 a_{3i} \qquad 2.85$$

which has the solution

$$c_i(z) = \left[\frac{\Phi_{1st}^2 + 2 a_{3i}}{\Phi_{1st}^2 \cosh(\Phi_{1st})} \right] \cosh(\Phi_{1st} z) - \frac{2 a_{3i}}{\Phi_{1st}^2} \qquad 2.86$$

with the center concentration given by

$$c_i(0) = \frac{\Phi_{1st} + [2 a_{3i}(\Phi_{1st} - \Phi_{1st} \cosh(\Phi_{1st})) / \Phi_{1st}^2]}{\Phi_{1st} \cosh(\Phi_{1st})} . \qquad 2.87$$

This form of the expression permits ready comparisons with the similar expressions for cylindrical and spherical coordinates, Table 2.7 and 2.8. (The functions $\Phi_{1st}^2 \cosh(\Phi_{1st}^2)$, $\sinh(\Phi_{1st}^2)$, and $\Phi_{1st}^2 I_o(\Phi_{1st}^2)$ in Table 2.7 all have series expansions in odd powers of Φ_{1st}^2 only, beginning with the same first-order term.) In the limit of small Φ_{1st}^2, a_{3i} also goes to zero, thus $c_i(O)$ goes to one in this limit as expected. For some neighborhood of a_{1i} about zero, this expression can be used to estimate $c_i(0)$ for second-order cases. Tables 2.7 and 2.8 also give the dimensionless concentration profiles and center concentrations

for the Robin's problem in all three coordinate systems. The general Robin's problem

is discussed in Chapter Four, but solutions for the first-order subcase are included here

for convenience. The internal effectiveness factor is also defined more formally than in

Chapter One by

$$\eta_{int} = \frac{(p+1)D_i \hat{c}_{is}\left(\dfrac{dc_i}{dz}\right)_{z=1}}{L^2 r_p(\hat{c}_{is}, \hat{c}_{js}, ..)} \qquad 2.88$$

where p is zero for a slab, one for a cylinder and two for a sphere; see Aris (1975) or

Lee (1985) for general details. For the slab-like medium, the solution is

$$\eta_{int} = \frac{\tanh(\Phi_{1st})}{\Phi_{1st}}, \qquad a_{1i} = 0, \qquad \Psi = 0 \qquad 2.89$$

which is identical in form to those for simple first-order irreversible or reversible kinetics

in Cartesian coordinates, Chapter One. When $a_{1i} = 0$, an analytical solution to the

reduced first-order kinetics problem can be derived in spherical or cylindrical coordinate

systems as well. Internal effectiveness factors for the three common geometries are

given in Table 2.9 for the Dirichlet and Robin's problem.

It is worth noting that, given fixed surface concentrations, temperature could, in

theory, be manipulated for Cases I-III, such that $a_{1i} = 0$, through temperature's effect

Table 2.7 Degenerate First-Order Concentration Profiles

Dirichlet Problem	$c_i(z)$

Slab

$$\left[\frac{\Phi_{1st}^2 + 2a_{3i}}{\Phi_{1st}^2 \cosh(\Phi_{1st})}\right]\cosh(\Phi_{1st}z) - \frac{2a_{3i}}{\Phi_{1st}^2}$$

Cylinder

$$\left[\frac{\Phi_{1st}^2 + 2a_{3i}}{\Phi_{1st}^2 I_0(\Phi_{1st})}\right]I_0(\Phi_{1st}z) - \frac{2a_{3i}}{\Phi_{1st}^2}$$

Sphere

$$\left[\frac{\Phi_{1st}^2 + 2a_{3i}}{\Phi_{1st}\sinh(\Phi_{1st})}\right]\frac{\sinh(\Phi_{1st}z)}{\Phi_{1st}z} - \frac{2a_{3i}}{\Phi_{1st}^2}$$

Robin's Problem

Slab

$$\left[\frac{Bi_m(1 + 2a_{3i}/\Phi_{1st}^2)}{\Phi_{1st}\sinh(\Phi_{1st}) + Bi_m\cosh(\Phi_{1st})}\right]$$

$$\cdot\cosh(\Phi_{1st}z) - 2a_{3i}/\Phi_{1st}^2$$

Cylinder

$$\left[\frac{Bi_m(1 + 2a_{3i}/\Phi_{1st}^2)}{\Phi_{1st}I_1(\Phi_{1st}) + Bi_m I_0(\Phi_{1st})}\right]$$

$$\cdot I_0(\Phi_{1st}z) - 2a_{3i}/\Phi_{1st}^2$$

Sphere

$$\left[\frac{Bi_m(1 + 2a_{3i}/\Phi_{1st}^2)}{\cosh(\Phi_{1st}) + \frac{(Bi_m - 1)}{\Phi_{1st}}\sinh(\Phi_{1st})}\right]$$

$$\cdot\frac{\sinh(\Phi_{1st}z)}{\Phi_{1st}z} - \frac{2a_{3i}}{\Phi_{1st}^2}$$

Table 2.8 Degenerate First-Order Midplane Concentrations

Dirichlet Problem	$c_i(0)$

Slab

$$\frac{\Phi_{1st} + 2a_{3i}[\Phi_{1st} - \Phi_{1st}\cosh(\Phi_{1st})]/\Phi_{1st}^2}{\Phi_{1st}\cosh(\Phi_{1st})}$$

Cylinder

$$\frac{\Phi_{1st} + 2a_{3i}[\Phi_{1st} - \Phi_{1st}I_o(\Phi_{1st})]/\Phi_{1st}^2}{\Phi_{1st}I_o(\Phi_{1st})}$$

Sphere

$$\frac{\Phi_{1st} + 2a_{3i}[\Phi_{1st} - \Phi_{1st}\cosh(\Phi_{1st})]/\Phi_{1st}^2}{\sinh(\Phi_{1st})}$$

Robin's Problem

Slab

$$\frac{1 + 2a_{3i}/\Phi_{1st}^2}{\cosh(\Phi_{1st}) + \dfrac{\Phi_{1st}}{Bi_m}\sinh(\Phi_{1st})} - \frac{2a_{3i}}{\Phi_{1st}^2}$$

Cylinder

$$\frac{1 + 2a_{3i}/\Phi_{1st}^2}{I_0(\Phi_{1st}) + \dfrac{\Phi_{1st}}{Bi_m}I_1(\Phi_{1st})} - \frac{2a_{3i}}{\Phi_{1st}^2}$$

Sphere

$$\frac{1 + 2a_{3i}/\Phi_{1st}^2}{\dfrac{\sinh(\Phi_{1st})}{\Phi_{1st}} - \dfrac{\cosh(\Phi_{1st})}{Bi_m} - \dfrac{\sinh(\Phi_{1st})}{\Phi_{1st}Bi_m}} - \frac{2a_{3i}}{\Phi_{1st}^2}$$

on the forward and reverse rate constants, forcing first-order behavior to occur. No obvious benefit results.

Internal Effectiveness Factors of Second-Order Reactions

The internal effectiveness factor measures the ratio of actual consumption of a species inside a medium relative to the consumption possible in the absence of concentration gradients, i.e. at surface compositions. For the single reaction systems considered in this article, this expression is given in numerous texts including Aris (1975) and takes the following form for second-order systems in terms of c' or c''

$$\eta_{int} = \frac{\left(\frac{dc'}{dz}\right)_{z=1}}{\Psi} = \frac{\left(\frac{dc''}{dz}\right)_{z=1}}{-1} \qquad 2.90$$

where

$$\left(\frac{dc'}{dz}\right)_{z=1} = \pm\sqrt{-\frac{2c'(0)^3}{3} - \Phi_{1st}^2 c'(0)^2 - 2\Psi c'(0)} \qquad 2.91$$

where the sign is chosen to match the sign of Ψ, and where

$$\left(\frac{dc''}{dz}\right)_{z=1} = \pm\sqrt{\frac{2\Psi c''(0)^3}{3} - \Phi_{1st}^2 c''(0)^2 + 2c''(0)} \; . \qquad 2.92$$

Table 2.9 Degenerate First-Order Effectiveness Factors

Dirichlet Problem	η_{int}
Slab	$\dfrac{\tanh(\Phi_{1st})}{\Phi_{1st}}$
Cylinder	$\dfrac{2I_1(\Phi_{1st})}{\Phi_{1st}I_0(\Phi_{1st})}$
Sphere	$\dfrac{3}{\Phi_{1st}\tanh(\Phi_{1st})} - \dfrac{3}{\Phi_{1st}^2}$

Robin's Problem	η
Slab	$\dfrac{1}{\dfrac{\Phi_{1st}}{\tanh(\Phi_{1st})} + \dfrac{\Phi_{1st}^2}{Bi_m}}$
Cylinder	$\dfrac{2I_1(\Phi_{1st})}{\Phi_{1st}I_0(\Phi_{1st}) + \dfrac{\Phi_{1st}^2}{Bi_m}I_1(\Phi_{1st})}$
Sphere	$\dfrac{3\coth(\Phi_{1st}) - 3/\Phi_{1st}}{1 + \dfrac{\Phi_{1st}\coth(\Phi_{1st}) - 1}{Bi_m}}$

Alternatively, the dimensionless species' concentration eq. (2.88) can be used

$$\left(\frac{dc_i}{dz}\right)_{z=1} = \pm\sqrt{4a_{1i}(1 - c_i^3(0)) + 6a_{2i}(1 - c_i^2(0)) + 4a_{3i}(1 - c_i(0))} \qquad 2.93$$

The remaining portion of eq. (2.88) for the internal effectiveness factor can also be expressed in terms of the a_{ij}. The external dimensionless rate occurs at $c_i = 1$, the surface concentration, in the right-hand side of eq. (2.18). It can be shown that the internal effectiveness factor is given by

$$\eta_{int} = \frac{(p+1)\left(\dfrac{dc_i}{dz}\right)_{z=1}}{6a_{1i} + 6a_{2i} + 2a_{3i}} \ . \qquad 2.94$$

Table 2.10 gives the expression in the denominator for each species in all seven cases for the slab-like geometry (p = 0). It should be observed that although a_{1i}, a_{2i} and a_{3i} vary from species to species within a case when using these expressions, Φ_{1st}^2 and Ψ do not, and η_{int} can be determined from these alone, rather than the a_{ij}! No species dependence is suggested for η_{int}.

Methods exist for estimating the internal effectiveness factor based on the generalized Thiele modulus approach, Lee (1985), Aris (1975). The asymptotic form of the internal effectiveness factor based on a generalized Thiele modulus is often sufficiently accurate for engineering requirements. This expression matches the asymptotic behavior at both the diffusion free and diffusion dominated limits, but is

Table 2.10 Denominators for the Internal Effectiveness Factor Expression

Case	Species	$(dc_i/dz)_{z=1}$ / η_{int}
I	A	$\Phi^2_{B+A} - \Phi^2_{R+P}/\Gamma_{AP}$
I	B	$\Phi^2_{A+B} - \Phi^2_{A+B}\Phi^2_{R+P}/\Gamma_{AP}\Phi^2_{B+A}$
I	P	$\Phi^2_{R+P} - \Gamma_{AP}\Phi^2_{B+A}$
I	R	$\Phi^2_{P+R} - \Gamma_{AP}\Phi^2_{B+A}\Phi^2_{P+R}/\Phi^2_{R+P}$
II	A	$2\Phi^2_{2A} - 2\Phi^2_{R+P}/\Gamma_{AP}$
II	P	$\Phi^2_{R+P} - \Gamma_{AP}\Phi^2_{2A}$
II	R	$\Phi^2_{P+R} - \Gamma_{AP}\Phi^2_{2A}\Phi^2_{P+R}/\Phi^2_{R+P}$
III	A	$2\Phi^2_{2A} - 2\Phi^2_{2P}/\Gamma_{AP}$
III	P	$2\Phi^2_{2P} - \Gamma_{AP}\Phi^2_{2A}$
IV	A	$\Phi^2_{B+A} - \Phi^2_P/\Gamma_{AP}$
IV	B	$\Phi^2_{A+B} - \Phi^2_{A+B}\Phi^2_P/\Gamma_{AP}\Phi^2_{B+A}$
IV	P	$\Phi^2_P - \Gamma_{AP}\Phi^2_{B+A}$
V	A	$2\Phi^2_{2A} - 2\Phi^2_P/\Gamma_{AP}$
V	P	$\Phi^2_P - \Gamma_{AP}\Phi^2_{2A}$
VI	A	Φ^2_{B+A}
VI	B	Φ^2_{A+B}
VII	A	$2\Phi^2_{2A}$

uncertain, and not guaranteed to be even approximately correct, in intermediate ranges. Conventional approaches to estimating midplane concentrations are observed to fail badly, although limiting asymptotes of the internal effectiveness factor are usually approximately correct. This is unfortunate, since the internal effectiveness factor for the slab geometry can be written as an algebraic function of the *ab initio* known parameters plus the midplane concentration. The slab midplane concentration is immediately available from the new analytical solution presented here, plus the analysis suggests several new ways to estimate it under various limiting situations.

Separate plots of the internal effectiveness factor versus the relevant irreversible reaction Thiele moduli can be prepared for both Case VI and Case VII kinetics. Because these two irreversible reaction systems have been studied by others numerically, these plots will be presented here using the analytical solution. The results for these two cases are also part of the general plots of the internal effectiveness factor versus Φ_{1st}^2 and Ψ presented later. Internal effectiveness factors have been obtained numerically by Bischoff (1965) for the problem

$$D \frac{d^2 \hat{c}}{dx^2} = k' \hat{c}^n \qquad \qquad 2.95$$

where n is the reaction order and k' is a rate constant. This plot is given in many standard heterogeneous kinetics texts. The comparable problem in this paper, Case VII of Table 2.1, is

$$D_A \frac{d^2 \hat{c}_A}{dx^2} = 2 k_f \hat{c}_A^2 \qquad \qquad 2.96$$

with the two fundamental moduli given by

$$\Phi_{1st}^2 = \frac{4L^2 k_f \hat{c}_{As}}{D_A} \qquad \Psi = \frac{\Phi_{1st}^4}{4} = \frac{4L^4 k_f^2 \hat{c}_{As}^2}{D_A^2} \; . \qquad 2.97$$

There is really only a single parameter, since Φ_{1st} and Ψ are related. It is almost certainly the best known simultaneous second-order reaction and diffusion problem result. Plots of η_{int} are made in Bischoff versus a generalized Thiele modulus, Φ_G, given by

$$\Phi_G^2 = \frac{L^2(n+1)k'\hat{c}_s^{n-1}}{2D} = \frac{L^2 3(2k_f)\hat{c}_{As}}{2D_A} = 4.5a_{1A} \qquad 2.98$$

modified here to match the current nomenclature and to coincide with second-order reaction systems. A feature of the generalized Thiele modulus development is that

$$\eta_{int} \rightarrow \frac{1}{\Phi_G} \qquad \Phi_G \rightarrow \infty \; . \qquad 2.99$$

Noting that k' = 2k$_f$, substitution of eqs. (2.97) and (2.98) into eq. (2.99) yields

$$\eta_{int} \rightarrow \frac{2}{\sqrt{3\,\Phi_{1st}^2}} \qquad \Phi_{1st} \rightarrow \infty \qquad 2.100$$

as the equivalent expression. Fig. 2.6 compares the exact solution for the irreversible power law kinetics of Case VII with an asymptotically correct expression based on the generalized Thiele modulus approach. The asymptotic curve is based on
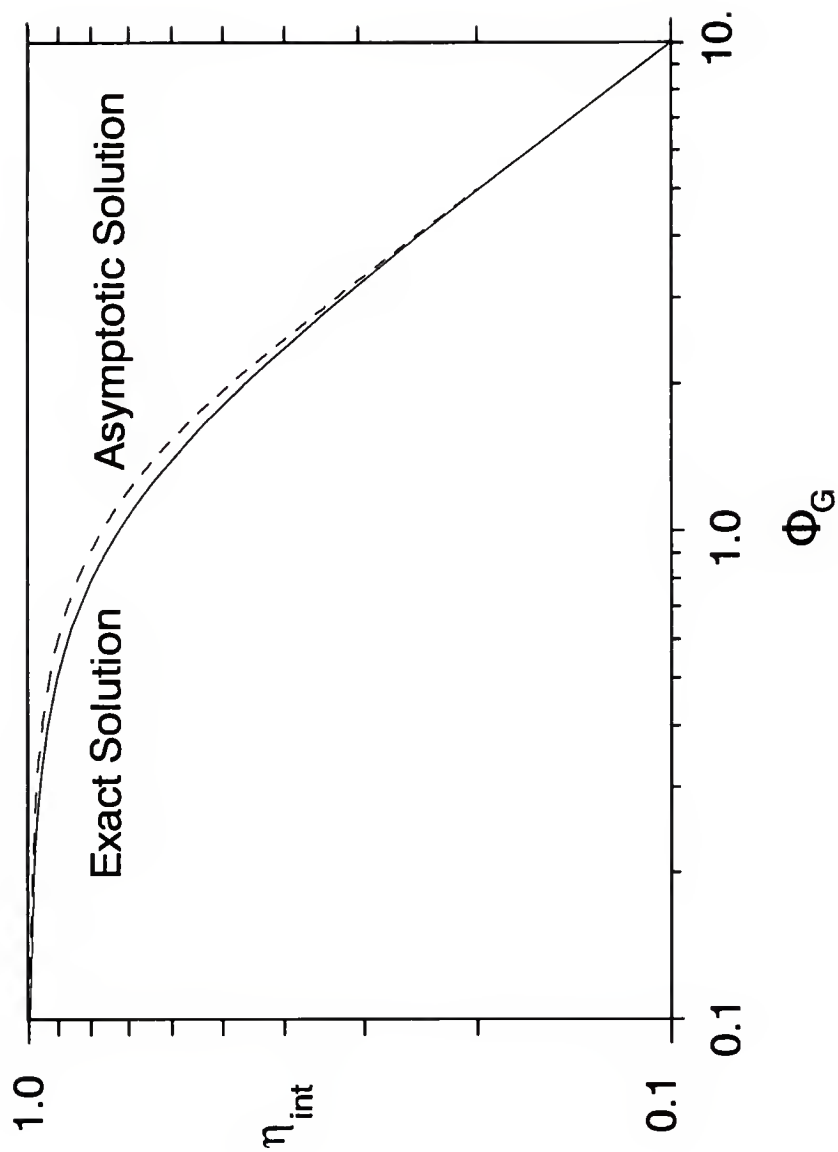
Figure 2.6 Departure of the exact solution from the asymptotically matched prediction for the irreversible single species second-order reaction.

$$\eta_{int} = \frac{\sqrt{1 - \left(\frac{\hat{c}_A(0)}{\hat{c}_{As}}\right)^3}}{\Phi_G} \qquad \qquad 2.101$$

$$\frac{\hat{c}_A(0)}{\hat{c}_{As}} = \frac{1}{\cosh\left(\sqrt{\frac{2\,\Phi_G^2}{3}}\right)} \cdot \qquad \qquad 2.102$$

Eq. (2.102) is an asymptotically consistent estimator derived from

$$\frac{\hat{c}(0)}{\hat{c}_s} = \frac{1}{\cosh\left(\sqrt{\frac{2\,\Phi_G^2}{n+1}}\right)} \qquad \qquad 2.103$$

which is the general nth-order power law kinetics analog. These expressions are

consistent estimators in the sense that for nth-order power law kinetics

$$\eta_{int} = \frac{\sqrt{2}}{Lk'\hat{c}_s^n}\sqrt{Dk'\frac{\hat{c}_s^{n+1} - \hat{c}(0)^{n+1}}{n+1}} = \frac{\sqrt{1 - \left(\frac{\hat{c}(0)}{\hat{c}_s}\right)^{n+1}}}{\Phi_G} \qquad \qquad 2.104$$

These expressions are easily derived from direct integration of the general power law kinetics governing equation and the definintion of the internal effectivness factor. The following Taylor series expansion can be made for eq. (2.103) raised to the (n + 1) power

$$\frac{1}{\cosh^{n+1}(\beta \, \Phi_G)} = 1 - \frac{(n+1) \, \beta^2 \, \Phi_G^2}{2!} + higher \; order \; terms \qquad 2.105$$

the free parameter, β, in eq. (2.105) is chosen such that

$$\eta_{int} \rightarrow 1 \qquad as \qquad \Phi_G \rightarrow 0 \qquad\qquad 2.106$$

The limit as Φ_G goes to infinity is automatically satisfied and does not constrain β. So β can be chosen as

$$\beta = \frac{n+1}{2!} \qquad\qquad 2.107$$

to satisfy eq. (2.106). The commonly cited estimator

$$\frac{\hat{c}(0)}{\hat{c}_s} = \frac{1}{\cosh(\Phi_G)} \qquad\qquad 2.108$$

suggested by earlier workers, e.g. Lee (1985), is clearly different and inconsistent with the asymptotic limits on the internal effectiveness factor, except for first-order reactions, and has been observed to fail badly as a consequence. The asymptotic method outlined here, however, never overestimates the Case VII effectiveness factor by more than 7%. Note that the asymptotic method and the exact method have different conventions for the

kinetic rate constant, since power law kinetic studies have tended to lump the stoichiometric coefficient and the rate constant. Allowances have been made for this factor throughout the preceeding discussion.

Figure 2.7 is a three dimensional perspective plot of η_{int} versus Φ_{A+B} and Φ_{B+A} for the kinetics of Table 2.1, Case VI, A + B $\rightarrow$ products. The surface is symmetric about the line $\Phi_{A+B} = \Phi_{B+A}$. About 95% of the surface was calculated using the Weierstrass Pe-function expansion in eq. (2.56) in the analytical solution, but the lowest η_{int} values coincide with prohibitively large invariant magnitudes in some regions, such that the discriminant of the canonical polynomial is nearly zero. In those cases, an asymptotic equation, either (2.67) or (2.68), was used instead to complete the surface. This led to negligible errors that were well below the resolution of the graph. The affected regions were those where one irreversible reaction Thiele modulus was small and the other was large. Such situations are asymptotic to first-order behavior in the governing differential equation. It can be seen that either Φ_{A+B} or Φ_{B+A} effects η_{int} much like a generalized Thiele modulus, or a first-order modulus, when the other modulus is small. The line $\Phi_{A+B} = \Phi_{B+A}$ has physical significane exactly analogous to Case VII kinetics in terms of Φ_{2A}^2. When A = B, $v_A = v_B = 2$, then $\Phi_{1st}^2 = 2\Phi_{A+B}^2 + 2\Phi_{B+A}^2 = 4\Phi_{2A}^2$. Values of either Φ_{A+B}^2 or Φ_{B+A}^2 along the axis in Figure 2.7 would thus correspond to $\Phi_{2A}^2/2$. This is also the asymptote in the plane of the diagonal parameter space boundary given by $\Psi = \Phi_{1st}^4/4$ and shown along the top left edge of Figure 2.8. The constraint, $\Psi = \Phi_{1st}^4/4$, is always satisfied by the irreversible reaction, 2A $\rightarrow$ products. The maximum η_{int} for constant Φ_{1st} is seen to occur in this plane in Figure 2.8. This asymptotic limit implies that species
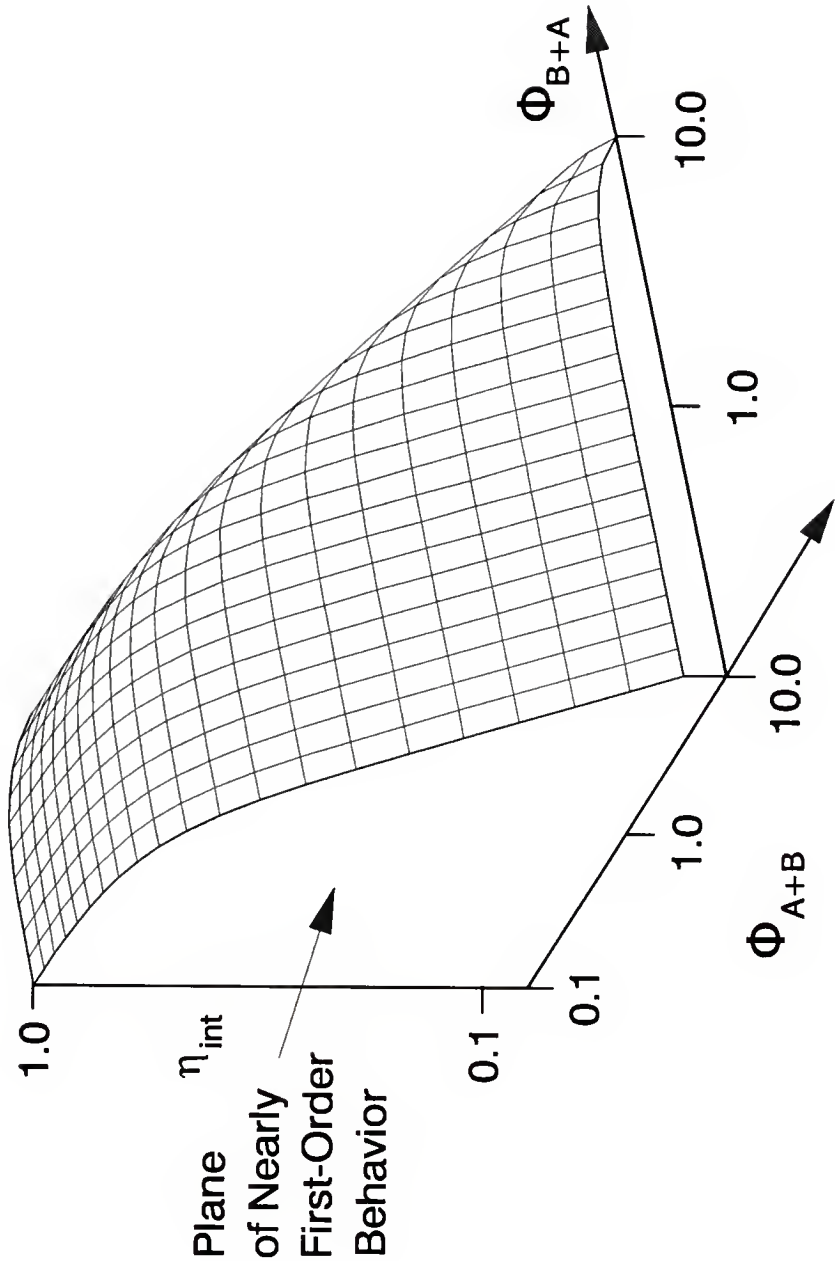
Figure 2.7 Internal effectiveness factor versus the two species moduli for the irreversible second-order reaction of two distinct species.
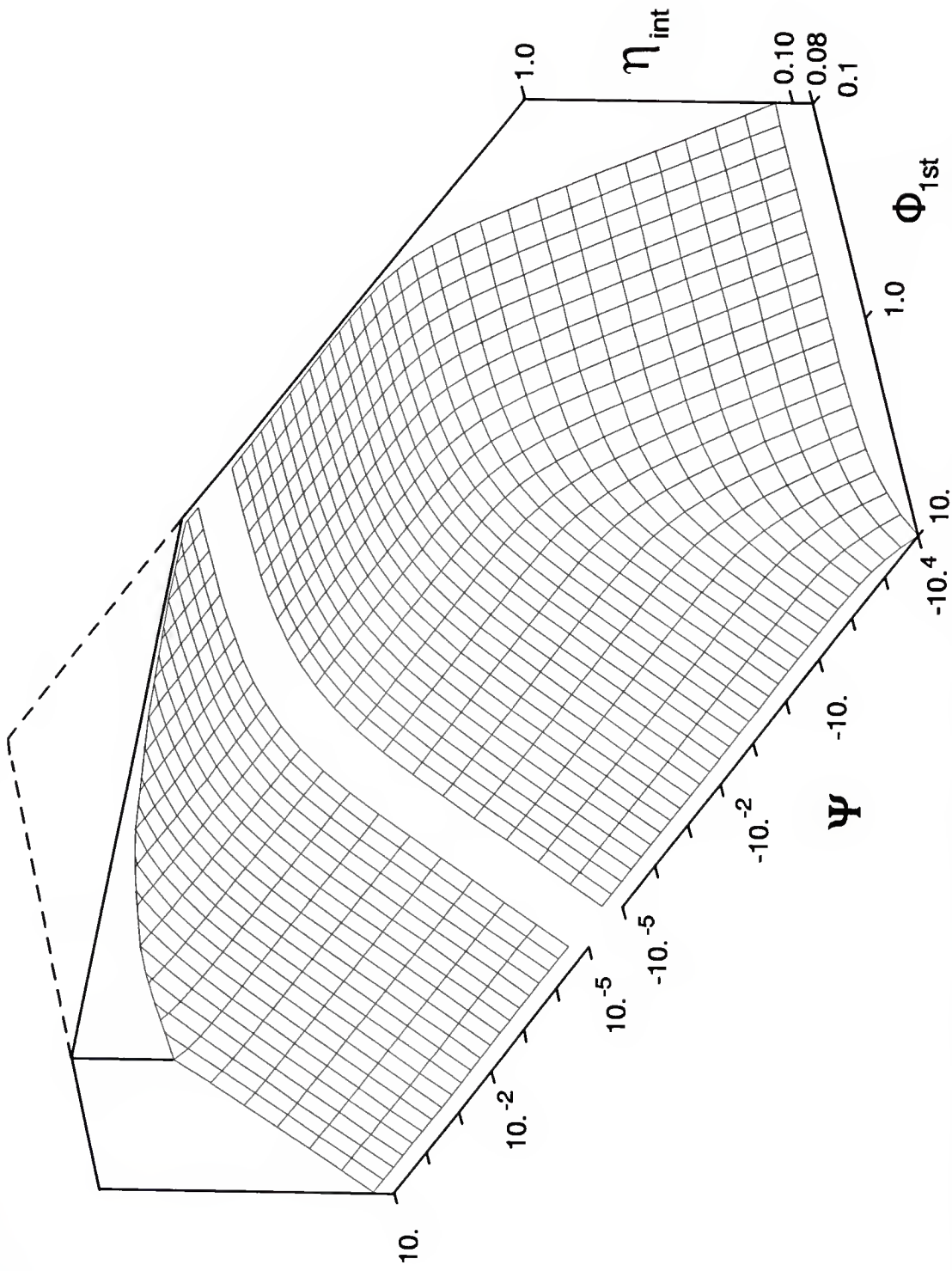
Figure 2.8 Triple log plot of the internal effectiveness factor versus the two fundamental parameters for second-order reaction and diffusion in a slab.

A is indistinguishable from species B from the perspective of the reaction diffusion problem.

Figure 2.8 presents a graph of the internal effectiveness factor, η_{int}, versus Φ_{1st} and Ψ. The parameter ranges plotted cover the transition from diffusion free to diffusion limited behavior which is the region of greatest interest. The internal effectiveness factor is given in terms of the two parameters and $c''(0)$ by the deceptively simple relationship

$$\eta_{int} = \sqrt{2\Psi c''(0)^3/3 - \Phi_{1st}^2 c''(0)^2 + 2c''(0)} \qquad 2.109$$

where $c''(0)$ in turn is a function of Φ_{1st} and Ψ, through eq. (2.41) and the boundary condition at $z = 1$. The limit, $|\Psi| \rightarrow 0$, leads to a first-order internal effectiveness factor, $\eta_{int} = \tanh(\Phi_{1st})/\Phi_{1st}$. This expression is approximately valid for small $|\Psi|$ like eq. (2.53) for the midplane concentration. The exact limit for a specified per cent accuracy varies with Φ_{1st}^2, but the poorest agreement occurs near $\Phi_{1st}^2 = 1$. Thus $|\Psi|$ is some measure of departure from first-order behavior. The internal effectiveness factor decreases as Ψ decreases from $\Phi_{1st}^4/4$ to zero to $-\infty$ and/or as Φ_{1st} increases. Values of the internal effectiveness factor at $\Psi = \pm 10^{-5}$ are virtually indistinguishable from the first-order limit, $\tanh(\Phi_{1st})/\Phi_{1st}$ at all values of Φ_{1st}^2. A generally diffusion free region can be defined for $\Phi_{1st} < 0.3$ and $|\Psi| < 0.0144$. A region of strong diffusional resistance could be defined for $\Phi_{1st} > 3.0$ or $|\Psi| > 144$.

Several types of asymptotic behavior are apparent in Figure 2.8. As $c''(0)$ approaches its upper bound in eq. (2.47), the expression for $c''_{eq}(z=0)$ can be inserted into eq. (2.100) to give, after some manipulation

$$\eta_{int} \rightarrow \sqrt{\frac{-\Phi_{1st}^6 + 6\Phi_{1st}^2\Psi + (\Phi_{1st}^4 - 4\Psi)^{1.5}}{6\Psi^2}} \qquad 2.110$$

The three asymptotic relationships with a single parameter below follow from this expression by limit processes. Eq. (2.113) below is noteworthy as the analog to the limiting expression for the irreversible second-order reaction, $2A \rightarrow$ products, $\eta_{int} \rightarrow 1/\Phi_G$, discussed in many textbooks and reexamined above. The right-hand side in eq. (2.110) satisfies the definition of the inverse of a generalized Thiele modulus, Φ_G, but a plot of η_{int} versus Φ_G would not be a line except at the asymptotic limits of η_{int} equal to unity and $1/\Phi_G$.

$$\eta_{int} \rightarrow \frac{1}{\Phi_{1st}} \qquad \Phi_{1st} \rightarrow \infty \qquad |\Psi| \rightarrow 0 \qquad 2.111$$

$$\eta_{int} \rightarrow \frac{2}{\sqrt[4]{-9\Psi}} \qquad \Phi_{1st} \rightarrow 0 \qquad \Psi \rightarrow -\infty \qquad 2.112$$

$$\eta_{int} \rightarrow \frac{2}{\sqrt{3\Phi_{1st}^2}} \qquad \Phi_{1st} \rightarrow \infty \qquad \Psi = \frac{\Phi_{1st}^4}{4} \qquad 2.113$$

$$\eta_{int} \rightarrow 1 \qquad \Phi_{1st} \rightarrow 0 \qquad |\Psi| \rightarrow 0 \qquad 2.114$$

Note in this regard that $\Phi_{1st}^4/4 \geq \Psi > -\infty$. The first asymptotic relationship, eq. (2.111), is an analog to first-order behavior, Chapter One. The fourth relationship, eq.

(2.114), is the parameterless diffusion free limit. Eq. (2.112) emphasizes that it is not sufficient for Φ_{1st} alone to be small for η_{int} to approach unity. Eq. (2.113) was derived earlier during the analysis of Case VII kinetics. Eqs. (2.112) and (2.113) lie along the feasible parameter space boundary in Figure 2.8 and this fact gains further relevance below.

The conventional definition of the generalized Thiele modulus, when applied to the governing equation for either c' or c'', leads to the following definition for conventional second-order systems

$$\Phi_G^2 = \frac{6\Psi^2}{-\Phi_{1st}^6 + 6\Phi_{1st}^2\Psi + (\Phi_{1st}^4 - 4\Psi)^{1.5}} \qquad 2.115$$

where the integration was made from the dimensionless diffusion modified reaction equilibrium concentration to the surface concentration (zero for both cases). The information contained in Figure 2.8 can be put on a graph of η_{int} versus Φ_G. What is obtained for conventional reversible and irreversible second-order reactions is a banded region lying between the curves for n=2 and $\Phi_{1st}=0$, Figure 2.9, that is asymptotic to unity in the limit of small Φ_G, and is asymptotic to $1/\Phi_G$ in the limit of large Φ_G. This is a predictable result, Aris (1965). One convenient feature of the generalized Thiele modulus is that it is possible to present results for any arbitrary kinetics and retain the asymptotic matching. This provides a setting for rating the relative effectiveness of different reactions or parameter ranges within a reaction. In the context of Figure 2.9, irreversible second-order reactions all have internal effectiveness factors less than that
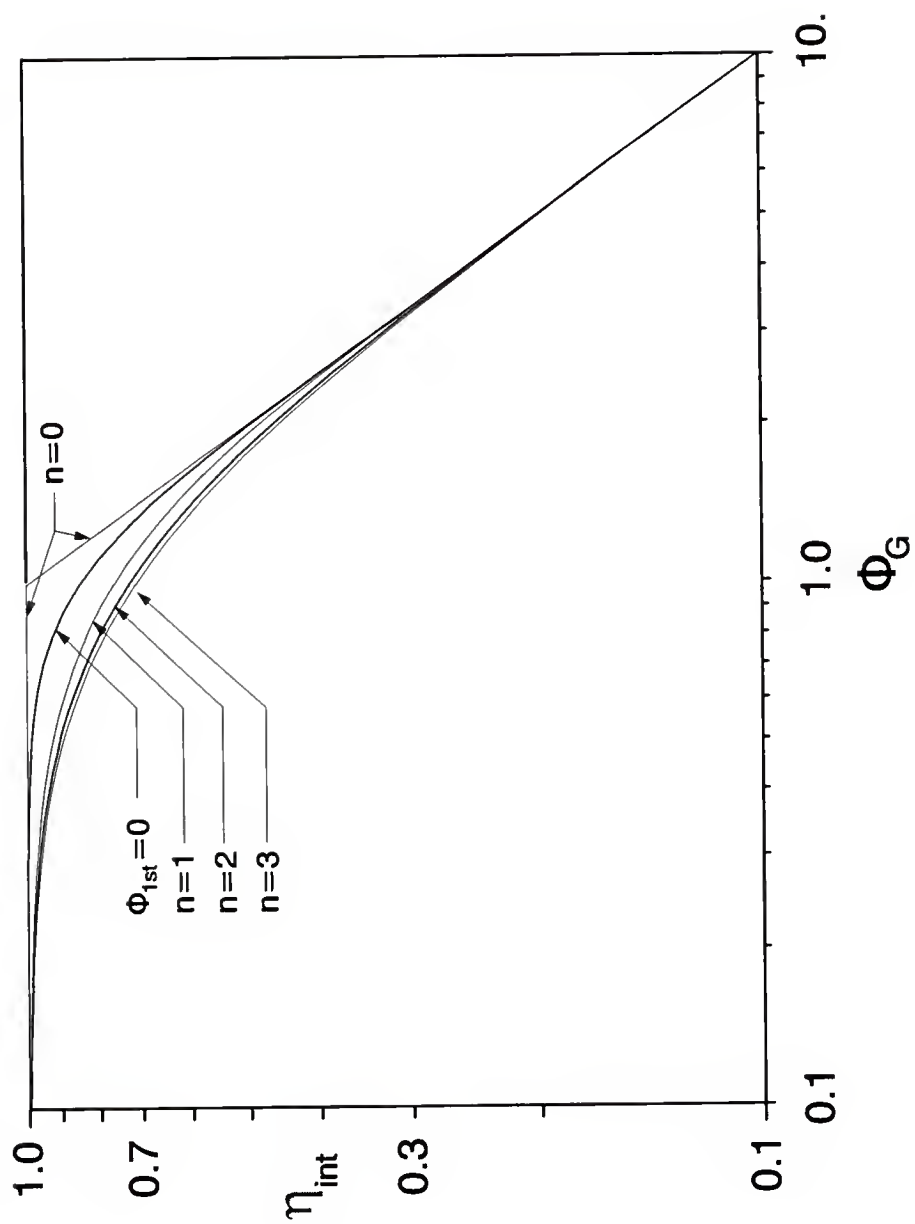
Figure 2.9 Internal effectiveness factors of second-order reversible reactions lie between the curves for n=2 and for $\Phi_{1st}=0$.

of a first-order reaction, i.e. between the curves for n = 2 and n = 1 power law kinetics indicated on the graph. Reversible second-order reactions exist throughout the entire banded region and are responsible for extending it well above the curve for first-order behavior. In this context it is fair to say that the irreversible reaction, $2A \rightarrow$ products, has the lowest internal effectiveness factor at constant generalized Thiele modulus. The region above the curve for n = 1 and the two intersecting lines $\eta_{int} = 1$ and $\eta_{int} = 1/\Phi_G$ can be filled with curves of positive fractional order reactions, i.e. $0 < n < 1$, in eq. (2.106), so certain reversible second-order reactions behave like fractional order reactions in the context of the reaction diffusion problem.

A few observations need to be emphasized here with respect to the asymptotic behavior of the internal effectiveness factor. First, the reaction becomes diffusion limited when either Φ_{1st} or $|\Psi|$ becomes large, whereas both moduli must be small for diffusion free reactions. Second, the asymptotic values of the internal effectiveness factor when $\Phi_{1st} \rightarrow 0$ are not unity, but are determined by Ψ, when the interdependence of Ψ and Φ_{1st} on similar irreversible Thiele moduli is ignored. How this could occur was discussed previously in this chapter.

The minimum of η_{int} at constant Φ_G occurs when $\Psi = \Phi_{1st}^4/4$. This minimum is always in effect for the irreversible reaction, $2A \rightarrow$ products. The minimum occurs for the irreversible reaction, $A+B \rightarrow$ products, when $D_A \hat{c}_{As} = D_B \hat{c}_{Bs}$. The minimum is never available to reversible reactions such as $A+B \rightleftarrows P+R$. By examining special cases of the general second-order reaction such as Cases III and VI of Table 2.1, it is possible to identify physical processes which tend to influence η_{int}. From Case VI, $D_A \hat{c}_{As} \neq D_B \hat{c}_{Bs}$

leads to an increase in η_{int} at constant Φ_G. This can be attributed to a diffusivity mismatch between reactants driving an enhancement of the intrinsic kinetic rate over that which would obtain if $D_A\hat{c}_{As} = D_B\hat{c}_{Bs}$. For this reaction the following relations hold

$$\Phi^2_{1st} = L^2 k_f (\hat{c}_{As}/D_B + \hat{c}_{Bs}/D_A) \qquad\qquad 2.116$$

$$\Psi = L^4 k_f^2 \hat{c}_{As} \hat{c}_{Bs}/D_A D_B \qquad\qquad 2.117$$

$$\Phi^4_{1st}/4 = L^4 k_f^2 (\hat{c}^2_{As}/D_B^2 + \hat{c}^2_{Bs}/D_A^2 + 2\hat{c}_{As}\hat{c}_{Bs}/D_A D_B)/4. \qquad\qquad 2.118$$

The internal effectiveness factor for Case VI is in the plane $\Psi = \Phi^4_{1st}/4$ only when $D_A\hat{c}_{As} = D_B\hat{c}_{Bs}$. In all other cases $\Psi < \Phi^4_{1st}/4$. The equality, $D_A\hat{c}_{As} = D_B\hat{c}_{Bs}$, can be interpreted as a diffusivity weighted stoichiometric condition for the reaction in the slab. For example, deviation of $\hat{c}_{Bs}$ from $D_A\hat{c}_{As}/D_B$ leads to an intraslab concentration profile mismatch between $\hat{c}_A$ and $\hat{c}_B$, and a relative increase of local reaction rates compared to Case VII. The cumulative effect is to increase the reaction rate averaged over the slab relative to that at the surface, i.e. increase η_{int}. This does not imply that nearly equal surface concentrations are a poor choice, since a constrained maximum in r_p at the surface occurs for equal surface concentrations. (The constraint being an upper bound on the total surface concentration.) The reaction rate averaged over the slab is the product of the reaction rate at the surface and the internal effectiveness factor. The reaction rate at the surface is maximum when $\hat{c}_{As}=\hat{c}_{Bs}$, subject to $\hat{c}_{As} + \hat{c}_{Bs} = $ constant, while the maximum internal effectiveness factor at constant Φ^2_{1st} occurs at $\hat{c}_{Bs} = D_A\hat{c}_{As}/D_B$. If, for example, $D_A > D_B$, then the $\hat{c}_{Bs}$ that maximizes the product, $\hat{c}^*_{Bs}$, is constrained by

$$\hat{c}_{As} < \hat{c}_{Bs}^* < D_A\hat{c}_{As}/D_B \qquad D_A > D_B. \qquad 2.119$$

See Bailey (1971) for more details on the optimum. This example illustrates how a diffusivity mismatch between reactants can cause η_{int} to increase when $\Psi < \Phi_{1st}^4/4$, but Ψ is never negative for this irreversible reaction. Consequently, there must be at least one other factor that exerts a positive influence on η_{int}, since η_{int} increases even further at constant Φ_G for reversible reactions. Other factors will be considered below.

Two additional influential physical factors arise from a study of case III, $2A \rightleftarrows 2P$. A potential for a nonzero reverse reaction rate ($k_r \neq 0$) leads to an increase in the maximum allowable η_{int} at constant Φ_G. Decreasing values of the product diffusivity, D_P, reduce Ψ and η_{int} when the forward surface reaction rate, $k_f\hat{c}_{As}^2$, exceeds the reverse surface reaction rate, $k_r\hat{c}_{Ps}^2$, i.e. when A is the reactant species, then low product mobility tends to reduce η_{int}. For this reaction

$$\Phi_{1st}^2 = 4L^2 (k_f\hat{c}_{As}/D_A + k_r\hat{c}_{Ps}/D_P) \qquad 2.120$$

$$\Psi = 4L^4 (k_f/D_A^2 - k_r/D_P^2)(k_f\hat{c}_{As}^2 - k_r\hat{c}_{Ps}^2) \qquad 2.121$$

$$\frac{\Phi_{1st}^4}{4} = 4L^4\left[\left(\frac{k_f}{D_A^2} - \frac{k_r}{D_P^2}\right)(k_f\hat{c}_{As}^2 - k_r\hat{c}_{Ps}^2) + k_f k_r\left(\frac{\hat{c}_{As}}{D_P} + \frac{\hat{c}_{Ps}}{D_A}\right)^2\right]. \qquad 2.122$$

This problem is identical with the irreversible reaction $2A \rightarrow$ products in the limit as $k_r \rightarrow 0$. Furthermore, the forward reaction is free of the diffusivity mismatch problem just discussed, since there is only a single reactant species, A. As k_r increases from zero,

at constant D_P and $\hat{c}_{Ps}$, the natural effect is to both increase Φ_{1st} and to reduce Ψ away from $\Phi_{1st}^4/4$. Both effects tend to reduce η_{int}. As k_r approaches the smaller of $k_f D_P^2/D_A^2$ and $k_f \hat{c}_{As}^2/\hat{c}_{Ps}^2$, Ψ approaches zero and the solution tends toward first-order behavior as a function of Φ_{1st}. The first-order asymptote for η_{int} as $\Phi_{1st} \to \infty$ is $1/\Phi_{1st}$, or about 15% less than when k_r was zero. If the smaller number above was $k_f \hat{c}_{As}^2/\hat{c}_{Ps}^2$, then the reaction has reached equilibrium at the slab surface. Increasing k_r beyond this point reverses the net direction of the reaction.

Alternatively, if the smaller number above was $k_f D_P^2/D_A^2$, then k_r can still be conceptually increased without reversing the direction of the reaction. As this occurs, Ψ becomes negative, and η_{int} continues to increase at constant Φ_G. If $\hat{c}_{Ps}$ is near zero this process can continue for some time before reaching conditions that imply reaction equilibrium at the slab surface. The existence of a potentially nonzero reverse reaction rate tends to increase η_{int} at constant Φ_G. This normally manifests itself in both Φ_{1st}^2 and Ψ. At constant Φ_{2A}^2, as $k_r \hat{c}_{Ps}$ increases, Φ_{2P}^2 increases, and therefore Φ_{1st} increases and Ψ decreases. These effects oppose each other but tend to increase η_{int} when Φ_G remains constant. When $k_f \hat{c}_{As}^2 - k_r \hat{c}_{Ps}^2 > 0$ and $k_r/D_P^2 > k_f/D_A^2$, and if k_r is held constant, then either increasing $\hat{c}_{Ps}$ or decreasing D_P tends to reduce Ψ and increase Φ_{1st}, while causing a net increase Φ_G and a net reduction in η_{int}. Reversing one of the inequalities would tend to reverse the direction of the effect. For the inequalities as given, increasing $\hat{c}_{Ps}$ promotes the reverse reaction, while decreasing D_P inhibits diffusion of the product in the medium, increasing $\hat{c}_P$ on average in the slab. Thus, if the "product" species is able to diffuse more readily than the reactant, then the reverse reaction is inhibited by loss of

reacting product molecules to the surface, and the apparent internal effectiveness factor exceeds that for the irreversible reaction. Additional diffusivity related effects are expected when three or four reacting species are present.

Figures 2.10 and 2.11 present some contours from the surface of Figure 2.8. In Figure 2.10 the transition between the two limiting asymptotes for each Ψ is seen to occur within a relatively narrow band of Φ_{1st} values (roughly 0.5 to 6). Figure 2.11 shows similar behavior for each Φ_{1st}, given that the fourth root of $|\Psi|$ has roughly the same numerical significance as Φ_{1st}. Values of η_{int} calculated in the limit as $\Phi_{1st} \rightarrow 0$ are within 0.5% of the values obtained at $\Phi_{1st}^2 = 0.01$ Figure 2.12 highlights the asymmetry of η_{int} with respect to the sign of Ψ. There is an envelope of permissible Φ_{1st} values, bounded below by $(4\Psi)^{\frac{1}{4}}$, and the maximum η_{int} at constant Φ_{1st} occurs on this envelope in the cases studied.

Concluding Remarks

This chapter has taken the first step in greatly extending the number of kinetic schemes for which analytical solutions exist. The analysis unified 17 species dependent differential equations into a single two-parameter problem. While seven new kinetic schemes were explicitly discussed, the method can be used to analyze second-order with zeroth-order cases as well as second-order reactions in parallel with first-order reactions, see Chapter Four. The results presented here are at least partially valid for the case of a zeroth-order reverse reaction. Empirical rate laws developed as second-order polynomials in concentration are not subject to the parameter space restrictions derived
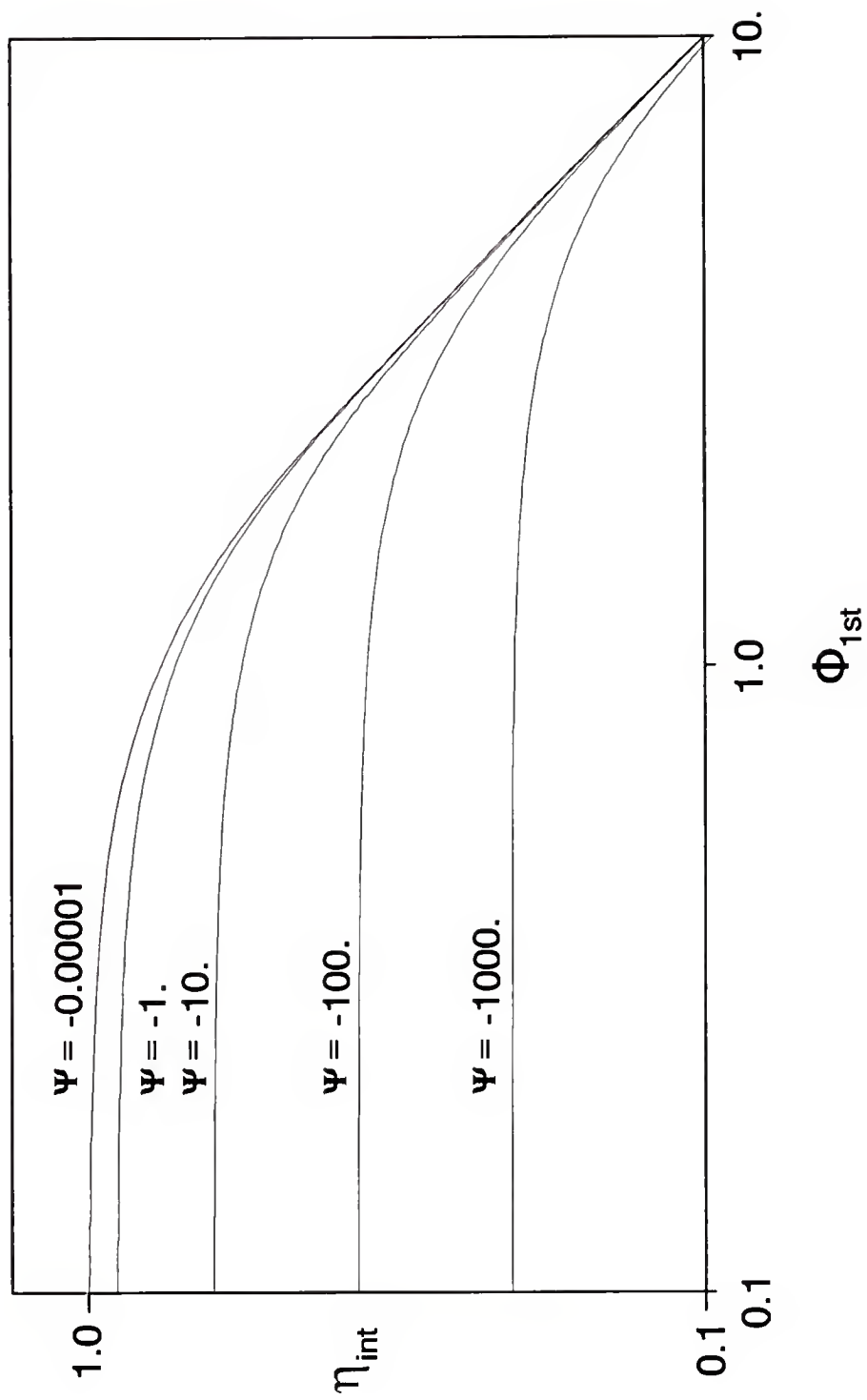
Figure 2.10 Log-log plot of internal effectiveness factor *vs.* Φ_{1st} for selected values of the second-order modulus, $\Psi < 0$.
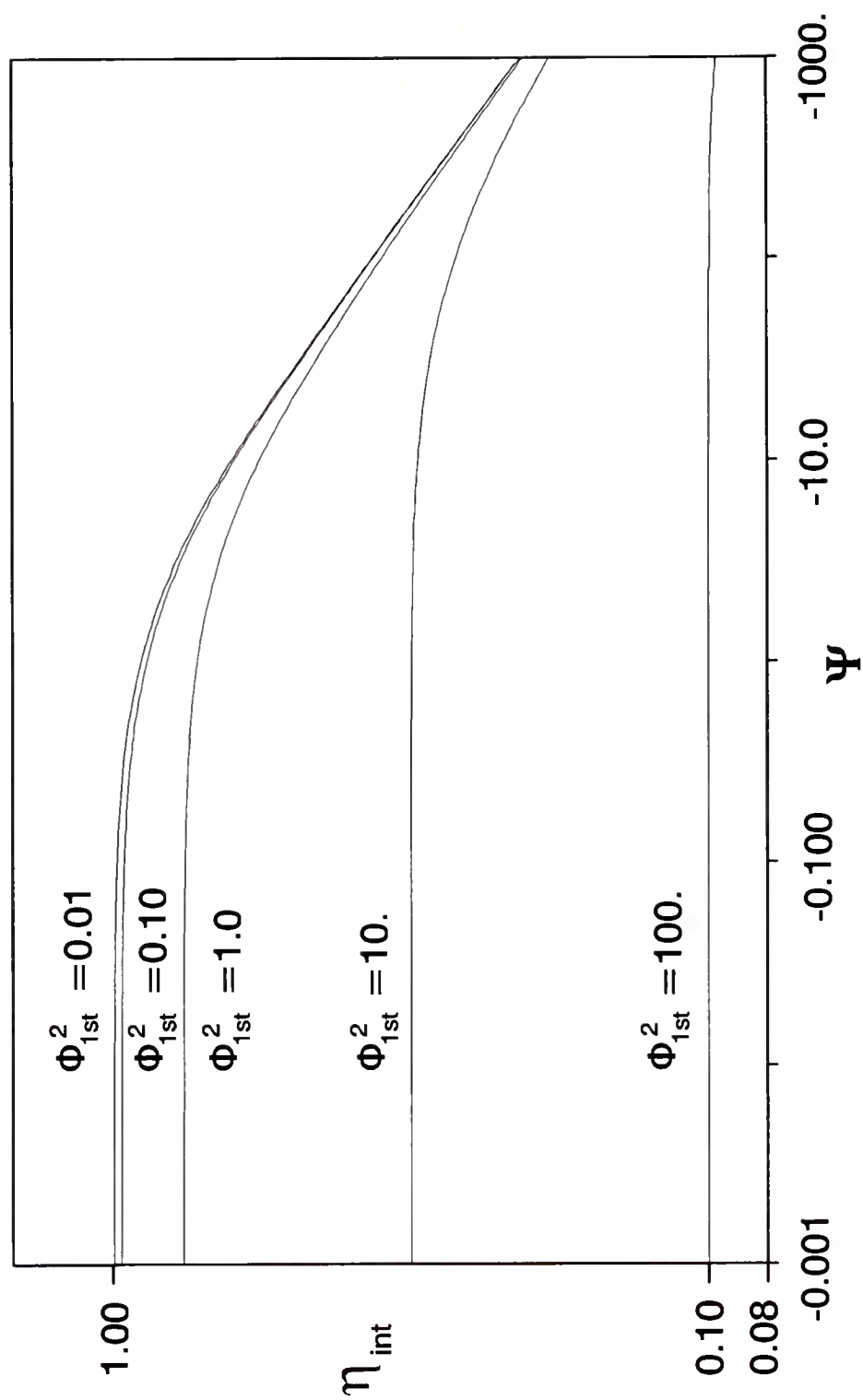
Figure 2.11 Log-log plot of the internal effectiveness factor vs. the second-order modulus, Ψ, for selected values of Φ_{1st}^2.
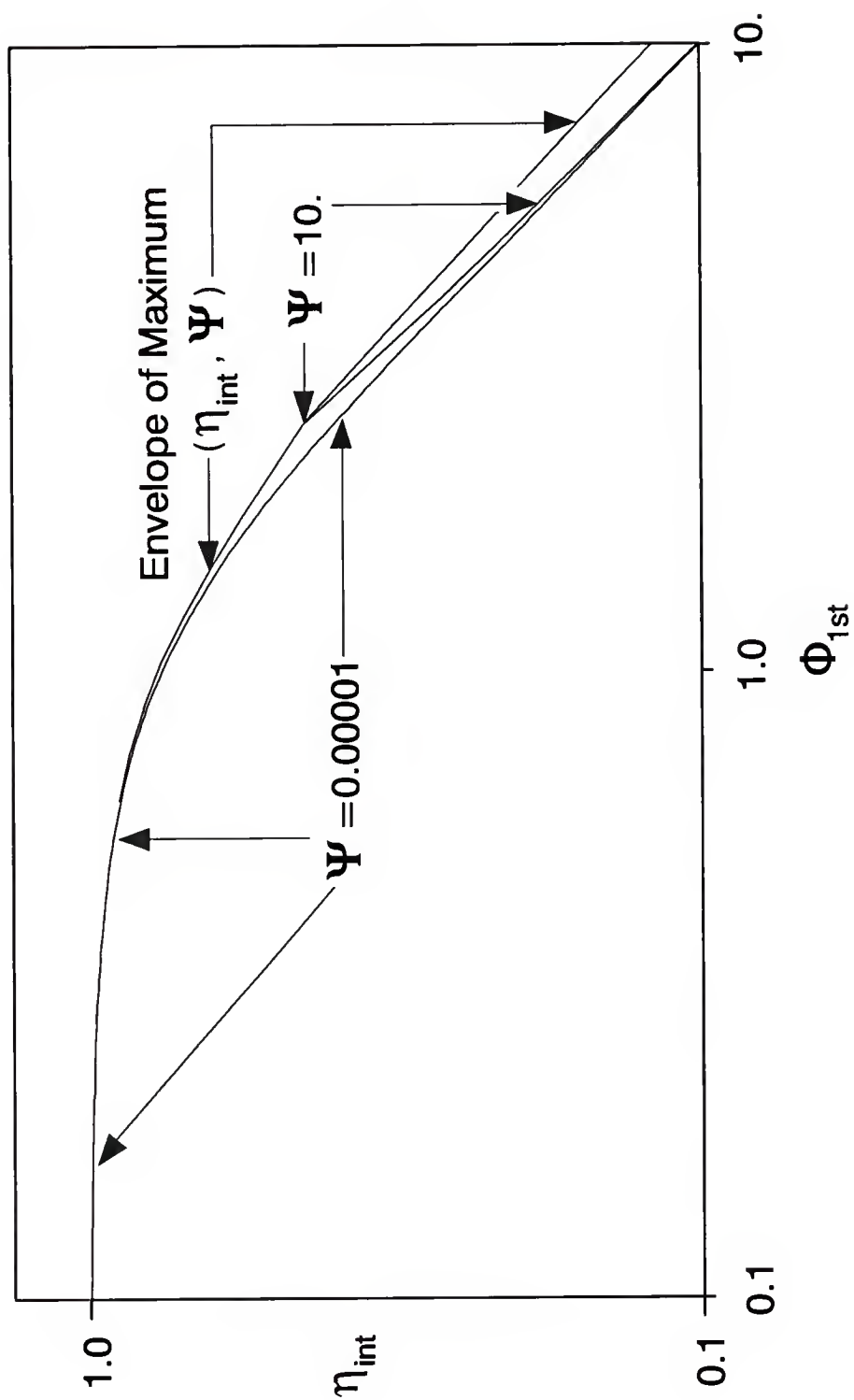
Figure 2.12 Log-log plot of the internal effectiveness factor vs. Φ_{1st} for two positive Ψ. Results approach a curve for $n = 1$ power law kinetics from above.

here for second-order elementary reactions. Quite unusual behavior is possible in regions of (Φ_{1st}^2, Ψ) outside that developed here. One example of this will be given in Chapter Four while examining autocatalytic reactions. Expressions for the concentration profiles in these cases will appear similar generally to those derived here. Problems can arise in defining a generalized Thiele modulus for empirical rate laws, since a zero of such a rate law may not be an actual equilibrium state for the reaction.

The effectiveness of shape normalization for second-order reactions in other geometries now warrants further study. The full extent of the restrictions that species multiplicity imposes on the moduli has not been characterized. The extension of the solution for the Dirichlet to the Robin's problem will be discussed in Chapter Four. The most useful of the different dimensionless concentration variables was c'', because of its numerical attributes. Its multiply constrained character made solution of the nonlinear equation that satisfies the final boundary condition simpler than would otherwise have been the case. There are other midplane concentration values, not physically feasible, that solve the nonlinear boundary value condition algebraic equation. These generally lie beyond the other equilibrium root of the reaction and diffusion equation, i.e. they are not a bifurcation phenomena, etc, but are simply infeasible physically. The location of the true solution was localized to a small interval with c'' as the dimensionless concentration. The reduction of the second-order reaction and diffusion problem to one with two parameters was a significant advance by itself, since this possibility escaped the notice of previous workers in the field. The parameter analysis for second-order kinetics used here for $\nabla^2 = d^2/dx^2$ applies to other forms of the Laplacian, such as those for

cylindrical and spherical coordinates. The two-parameter basis discussed here for rectangular coordinates provides a convenient setting for efficiently presenting numerical solution results in other coordinate systems.

CHAPTER 3
CONVENTIONAL THIRD-ORDER REACTION SYSTEMS

Introduction to Third-Order Reaction and Diffusion

In this chapter the presentation in Chapter Two will be extended to the case of the

third-order reaction and diffusion problem in a slab with the Dirichlet boundary

condition. A single analytical solution will be presented for a broad class of steady-state,

isothermal third-order reactions with diffusion in a slab-like medium with constant

diffusivities. All intrinsically third-order reversible and irreversible kinetic schemes can

be unified into a single three parameter problem. Analytical solutions for dimensionless

concentration profiles, internal effectiveness factors, etc. are determined as functions of

these three dimensionless parameters: a Thiele, or first-order, modulus, Φ_{1st}^2, a second-

order modulus, Ψ, and a new third-order modulus, X. This analysis provides semi-

quantitative conditions for both diffusion-free and diffusion-limited behavior. The

modulus, Ψ, will turn out to be especially adjustable by varying physical parameters.

Other limiting interrelationships between the parameters are developed that restrict the

size of the solution space in much the some way that Ψ was constrained by Φ_{1st}^2 in

Chapter Two. Only one published result on third-order behavior is known to the author.

This is the plot of internal effectiveness factor versus generalized Thiele modulus for the

case of n = 3 power law kinetics, Bischoff (1965), and generated here anew in Chapter One, Figure 1.3.

The solution procedure outlined in Chapter Two can be extended to reversible and irreversible third-order kinetic systems, which can have up to six species and reverse reactions of zeroth, first, second or third-order, so many permutations are possible. Analysis yielded a general three-parameter basis. Two of these parameters were fully analogous to the basis for the second-order problem in Chapter Two. This three-parameter basis size is larger than that actually required for the two irreversible reactions, 3A → products and 2A + B → products, which, in practice, require only one and two parameters respectively. In these two cases the three parameters are interrelated through two or one additional equations respectively. The addition of well over 20 new kinetic expressions, see Table 3.1, again more than doubles the number of elementary reactions possessing an analytical solution to the simultaneous reaction and diffusion problem from what was available after the developments in Chapter Two. The parameter space analysis and analytical solution procedure, plus expressions for the concentration profiles, internal effectiveness factors, etc. are presented below. Criteria for regions of strong diffusion control and nearly diffusion free operation are developed. Kinetic expressions other than those discussed here are solvable by the presented method.

Three-Parameter Equations and Concentration Profiles

The governing equation for one-dimensional, isothermal, steady-state, simultaneous reaction and diffusion for a species, i, with constant diffusivity, D_i, takes

Table 3.1 Typical Elementary Reactions With Intrinsically Third-Order Kinetics.

	Elementary Reaction	Rate Expression, r_P
1	$A + B + C \rightleftarrows P + R + Q$	$k_r \hat{c}_P \hat{c}_R \hat{c}_Q - k_f \hat{c}_A \hat{c}_B \hat{c}_C$
2	$2A + B \rightleftarrows P + R + Q$	$k_r \hat{c}_P \hat{c}_R \hat{c}_Q - k_f \hat{c}_A^2 \hat{c}_B$
3	$3A \rightleftarrows P + R + Q$	$k_r \hat{c}_P \hat{c}_R \hat{c}_Q - k_f \hat{c}_A^3$
4	$2A + B \rightleftarrows 2P + R$	$k_r \hat{c}_P^2 \hat{c}_R - k_f \hat{c}_A^2 \hat{c}_B$
5	$3A \rightleftarrows 2P + R$	$k_r \hat{c}_P^2 \hat{c}_R - k_f \hat{c}_A^3$
6	$3A \rightleftarrows 3P$	$k_r \hat{c}_P^3 - k_f \hat{c}_A^3$
7	$A + B + C \rightleftarrows P + R$	$k_r \hat{c}_P \hat{c}_R - k_f \hat{c}_A \hat{c}_B \hat{c}_C$
8	$2A + B \rightleftarrows P + R$	$k_r \hat{c}_P \hat{c}_R - k_f \hat{c}_A^2 \hat{c}_B$
9	$3A \rightleftarrows P + R$	$k_r \hat{c}_P \hat{c}_R - k_f \hat{c}_A^3$
10	$A + B + C \rightleftarrows 2P$	$k_r \hat{c}_P^2 - k_f \hat{c}_A \hat{c}_B \hat{c}_C$
11	$2A + B \rightleftarrows 2P$	$k_r \hat{c}_P^2 - k_f \hat{c}_A^2 \hat{c}_B$
12	$3A \rightleftarrows 2P$	$k_r \hat{c}_P^2 - k_f \hat{c}_A^3$
13	$A + B + C \rightleftarrows P$	$k_r \hat{c}_P - k_f \hat{c}_A \hat{c}_B \hat{c}_C$
14	$2A + B \rightleftarrows P$	$k_r \hat{c}_P - k_f \hat{c}_A^2 \hat{c}_B$
15	$3A \rightleftarrows P$	$k_r \hat{c}_P - k_f \hat{c}_A^3$
16	$A + B + C \rightleftarrows (k_r \neq 0)$	$k_r - k_f \hat{c}_A \hat{c}_B \hat{c}_C$
17	$2A + B \rightleftarrows (k_r \neq 0)$	$k_r - k_f \hat{c}_A^2 \hat{c}_B$
18	$3A \rightleftarrows (k_r \neq 0)$	$k_r - k_f \hat{c}_A^3$
19	$A + B + C \rightarrow$	$- k_f \hat{c}_A \hat{c}_B \hat{c}_C$
20	$2A + B \rightarrow$	$- k_f \hat{c}_A^2 \hat{c}_B$
21	$3A \rightarrow$	$- k_f \hat{c}_A^3$

the familiar form

$$D_i \frac{d^2 \hat{c}_i}{dx^2} = v_i r_P \qquad 3.1$$

where r_p is now a third-order rate of product formation kinetic expression possibly containing second, first or zeroth-order terms, see below, x is the length scale variable used throughout this work, and v_i is the stoichiometric coefficient for species i in the reaction. Recall that the boundary conditions for a conventional Dirichlet problem are

$$\hat{c}_i = \hat{c}_{is} \quad at \quad x = L \qquad 3.2$$

$$\frac{d\hat{c}_i}{dx} = 0 \quad at \quad x = 0 \qquad 3.3$$

where x = L is the exposed surface and x = 0 is the midplane of the slab. With these boundary conditions, all $\hat{c}_j$ can be expressed in terms of a single concentration, $\hat{c}_i$, by

$$\frac{D_i}{v_i} (\hat{c}_i - \hat{c}_{is}) = \frac{D_j}{v_j} (\hat{c}_j - \hat{c}_{js}). \qquad 3.4$$

Eq. (3.1) with a third-order r_p can be made dimensionless with eq. (3.4) and the following substitutions

$$c''(z) = \frac{D_i(\hat{c}_{is} - \hat{c}_i)}{L^2 v_i r_{Ps}} \qquad z = x/L \qquad\qquad 3.5$$

where r_{Ps} is r_P evaluated at $x = L$, the exposed surface. Some substitution of this general type is needed to reduce the parameter space to size three. This choice has certain desirable attributes outlined in Chapter Two. Eqs. (3.1-3.5) lead to a revised governing equation of the form

$$\frac{d^2c''}{dz^2} = Xc''^3 - \Psi c''^2 + \Phi_{1st}^2 c'' - 1 \equiv r''_P \qquad\qquad 3.6$$

with parameter free boundary conditions

$$\frac{dc''}{dz} = 0 \quad at \quad z = 0, \quad c''(1) = 0 \quad at \quad z = 1 \qquad\qquad 3.7$$

independent of the species, i, selected initially. In other words, c'' can be interpreted as either a universal dimensionless concentration for the problem or as a dimensionless extent of reaction. The third-order modulus, X, has physical similarity with Φ_{1st}^6, and the second-order modulus, Ψ, has physical similarity to Φ_{1st}^4 as noted in Chapter Two. For the six species third-order reversible reaction, $A + B + C \rightleftarrows P + R + Q$, with $r_P = k_r\hat{c}_P\hat{c}_R\hat{c}_Q - k_f\hat{c}_A\hat{c}_B\hat{c}_C$, these parameters are

$$X = L^6\left(\frac{k_r}{D_P D_R D_Q} + \frac{k_f}{D_A D_B D_C}\right)(k_r\hat{c}_{Ps}\hat{c}_{Rs}\hat{c}_{Qs} - k_f\hat{c}_{As}\hat{c}_{Bs}\hat{c}_{Cs})^2 \qquad 3.8$$

$$\Psi = L^4 \left(\frac{k_r \hat{c}_{Ps}}{D_R D_Q} + \frac{k_r \hat{c}_{Rs}}{D_P D_Q} + \frac{k_r \hat{c}_{Qs}}{D_P D_R} - \frac{k_f \hat{c}_{As}}{D_B D_C} - \frac{k_f \hat{c}_{Bs}}{D_A D_C} - \frac{k_f \hat{c}_{Cs}}{D_A D_B} \right) \qquad 3.9$$

$$(k_r \hat{c}_{Ps} \hat{c}_{Rs} \hat{c}_{Qs} - k_f \hat{c}_{As} \hat{c}_{Bs} \hat{c}_{Cs})$$

$$\Phi_{1st}^2 = L^2 \left(\frac{k_r \hat{c}_{Ps} \hat{c}_{Rs}}{D_Q} + \frac{k_r \hat{c}_{Rs} \hat{c}_{Qs}}{D_P} + \frac{k_r \hat{c}_{Qs} \hat{c}_{Ps}}{D_R} + \frac{k_f \hat{c}_{As} \hat{c}_{Bs}}{D_C} + \frac{k_f \hat{c}_{Bs} \hat{c}_{Cs}}{D_A} + \frac{k_f \hat{c}_{Cs} \hat{c}_{As}}{D_B} \right). \quad 3.10$$

The third-order reaction systems described in this chapter come in five broad classes. Within each class are various cases of species multiplicity. All five classes have a third-order reaction component. This is combined with one of the following: another third-order reaction in the reverse direction, a second-order reaction in the reverse direction, a first-order reaction in the reverse direction, a zeroth-order reaction in the reverse direction, or no reverse reaction at all. From the perspective of the analysis, it does not matter whether the reactants or the products participate in the "forward" third-order reaction, i.e. the reaction could be proceeding by a primarily first-order forward ("reverse") reaction with a weak third-order reverse ("forward") reaction. This is primarily a labelling problem, not an engineering problem. Table 3.1 lists 21 elementary reactions and the appropriate r_p. Listed below are general expressions for the three moduli for third-order reaction systems. These are based on a model kinetic expression:

$v_A A + v_B B + v_C C \rightleftarrows v_P P + v_R R + v_Q Q$, with forward and reverse rates constants, k_f

and k_r, rate of product formation expression, $r_P = k_r \hat{c}_P \hat{c}_R \hat{c}_Q - k_f \hat{c}_A \hat{c}_B \hat{c}_C$, characteristic length, L, diffusivities, D_i, and stoichiometric coefficients, v_i.

$$\Phi_{1st}^2 = L^2 \left(\frac{v_Q k_r \hat{c}_{Ps} \hat{c}_{Rs}}{D_Q} + \frac{v_P k_r \hat{c}_{Rs} \hat{c}_{Qs}}{D_P} + \frac{v_R k_r \hat{c}_{Qs} \hat{c}_{Ps}}{D_R} - \right.$$
$$\left. \frac{v_C k_f \hat{c}_{As} \hat{c}_{Bs}}{D_C} - \frac{v_A k_f \hat{c}_{Bs} \hat{c}_{Cs}}{D_A} - \frac{v_B k_f \hat{c}_{Cs} \hat{c}_{As}}{D_B} \right) \qquad 3.11$$

$$\Psi = L^4 \left(\frac{v_R v_Q k_r \hat{c}_{Ps}}{D_R D_Q} + \frac{v_P v_Q k_r \hat{c}_{Rs}}{D_P D_Q} + \frac{v_P v_R k_r \hat{c}_{Qs}}{D_P D_R} - \frac{v_B v_C k_f \hat{c}_{As}}{D_B D_C} - \right.$$
$$\left. \frac{v_A v_C k_f \hat{c}_{Bs}}{D_A D_C} - \frac{v_A v_B k_f \hat{c}_{Cs}}{D_A D_B} \right) (k_r \hat{c}_{Ps} \hat{c}_{Rs} \hat{c}_{Qs} - k_f \hat{c}_{As} \hat{c}_{Bs} \hat{c}_{Cs}) \qquad 3.12$$

$$X = L^6 \left(\frac{v_P v_R v_Q k_r}{D_P D_R D_Q} - \frac{v_A v_B v_C k_f}{D_A D_B D_C} \right) (k_r \hat{c}_{Ps} \hat{c}_{Rs} \hat{c}_{Qs} - k_f \hat{c}_{As} \hat{c}_{Bs} \hat{c}_{Cs})^2 \qquad 3.13$$

The ability to perform three types of empirical operations is sufficient to express the three parameters for a specific case from Table 3.1. These are to reduce the order of a reaction, to eliminate a reaction entirely (make irreversible), and to create species multiplicity at constant order. A reduction of order of one requires reducing the number of species in the elementary reaction by one. This is accomplished by picking a species, e.g. Q, and setting its stoichiometric coefficient to zero (equivalent to setting its diffusivity to infinity) and setting its surface concentration to unity in eqs. (3.11-3.13).

For example, the third-order/second-order system $A + B + C \rightleftharpoons P + R$ (all $v_i = \pm 1$) would yield

$$\Phi_{1st}^2 = L^2 \left(\frac{k_r \hat{c}_{Rs}}{D_P} + \frac{k_r \hat{c}_{Ps}}{D_R} + \frac{k_f \hat{c}_{As} \hat{c}_{Bs}}{D_C} + \frac{k_f \hat{c}_{Bs} \hat{c}_{Cs}}{D_A} + \frac{k_f \hat{c}_{Cs} \hat{c}_{As}}{D_B} \right) \qquad 3.14$$

$$\Psi = L^4 \left(\frac{k_r}{D_P D_R} - \frac{k_f \hat{c}_{As}}{D_B D_C} - \frac{k_f \hat{c}_{Bs}}{D_A D_C} - \frac{k_f \hat{c}_{Cs}}{D_A D_B} \right) (k_r \hat{c}_{Ps} \hat{c}_{Rs} - k_f \hat{c}_{As} \hat{c}_{Bs} \hat{c}_{Cs}) \qquad 3.15$$

$$X = L^6 \left(\frac{k_f}{D_A D_B D_C} \right) (k_r \hat{c}_{Ps} \hat{c}_{Rs} - k_f \hat{c}_{As} \hat{c}_{Bs} \hat{c}_{Cs})^2 . \qquad 3.16$$

The second operation, creating species multiplicity, is accomplished as follows. Everywhere that a species being converted from a unique species to a repeated species appears in eqs. (3.11-3.13) it must be replaced with the primary species. This includes surface concentrations, diffusivities, and stoichiometric coefficients. A change in the numerical value of the stoichiometric coefficient normally occurs during this operation as well. Seemingly repeated terms <u>must</u> be kept. For example consider the third-order reversible reaction $2A + B \rightleftharpoons 3P$, i.e. $C = A$ ($v_A = -2$) and $Q = R = P$ ($v_P = 3$). Then

$$\Phi_{1st}^2 = L^2 \left(\frac{9 k_r \hat{c}_{Ps}^2}{D_P} + \frac{4 k_f \hat{c}_{As} \hat{c}_{Bs}}{D_A} + \frac{k_f \hat{c}_{As}^2}{D_B} \right) \qquad 3.17$$

$$\Psi = L^4 \left(\frac{27 k_r \hat{c}_{Ps}}{D_P^2} - \frac{4 k_f \hat{c}_{As}}{D_A D_B} - \frac{4 k_f \hat{c}_{Bs}}{D_A^2} \right) (k_r \hat{c}_{Ps}^3 - k_f \hat{c}_{As}^2 \hat{c}_{Bs}) \qquad 3.18$$

$$X = L^6 \left(\frac{27 k_r}{D_P^3} + \frac{4 k_f}{D_A^2 D_B} \right) (k_r \hat{c}_{Ps}^3 - k_f \hat{c}_{As}^2 \hat{c}_{Bs})^2 . \qquad 3.19$$

To make the reaction irreversible, set k_r equal to zero everywhere in eqs. (3.11-3.13). Application of these rules gives appropriate expressions from third-order/third-order reversible reactions to the case of an irreversible first-order reaction (i.e. beyond problems requiring the Weierstrass elliptic Pe-function for solution). What about third-order or second-order reactions with a zeroth-order reverse reaction? For example, the reaction $3A \rightleftarrows$ ($k_r \neq 0$) and the above rules gives (taking $v_P = v_R = v_Q = 0$)

$$\Phi_{1st}^2 = L^2 \left(\frac{9 k_f \hat{c}_{As}^3}{D_A} \right) \qquad 3.20$$

$$\Psi = L^4 \left(- \frac{27 k_f \hat{c}_{As}}{D_A^2} \right) (k_r - k_f \hat{c}_{As}^3) \qquad 3.21$$

$$X = L^6 \left(\frac{27 k_f}{D_A^3} \right) (k_r - k_f \hat{c}_{As}^3)^2 . \qquad 3.22$$

These are the appropriate results for the three parameters. The problem is one of interpretation. If the zeroth-order reaction derives from some real chemical species, then its concentration should not become negative. Conventionally in the irreversible zeroth-

order reaction, the rate constant is set to zero at the position within the slab where this concentration vanishes, i.e. k_r is potentially discontinuous. This leads to a different boundary condition then was used in solving the general problem. An investigation into any equivalent problems for second-order or third-order systems with zeroth-order parts has not yet been done. So, the above general equations (3.11-3.13) are appropriate for deriving the parameter expansions for arbitrary mixtures of third-order, second-order, first-order and zeroth-order reactions, subject to the single caution concerning zeroth-order reactions, and cover cases that do not require solution by the Weierstrass Pe-function. In essence this is a general approach that could be standard for reactions of integer order, and used to teach the analytical solutions for problems from zeroth-order to third-order.

Eqs. (3.11-3.13) may be appropriate for nonelementary reactions such as $4A + 2B + 7C \rightleftarrows 4P + 5R$ that are fit to a third-order kinetic expression such as $k_r \hat{c}_P^2 \hat{c}_R - k_f \hat{c}_A \hat{c}_B \hat{c}_C$ in the sense that the defining relations for the three parameters were derived assuming arbitrary stoichiometric coefficients. The equations have not been tested against such seemingly exotic cases, and various interpretation problems of the above rules arise. Eqs. (3.11-3.13) were intended for the 21 cases of Table 3.1, as well as for the nine elementary cases of intrinsically second-order behavior in Table 2.1 and the three elementary cases of intrinsically first-order behavior (first-order reversible, first-order irreversible, and first-order reversible with zeroth-order).

The coefficients of c'' and c''^3 are clearly nonnegative for the conventional reactions being considered, while the sign of Ψ is more arbitrary. The first-order and

second-order moduli, Φ^2_{1st} and Ψ, are fully compatible with those developed for second-order reaction systems, see eqs. (2.45-2.46) in Chapter Two, under the rules above with $X = 0$. The first-order modulus, Φ^2_{1st}, reduces to the conventional Thiele modulus for either first-order irreversible or reversible reactions under these same rules, if $X = \Psi = 0$. The first-order modulus is usually different from the generalized, or normalized, Thiele modulus defined in Aris (p. 113, 1975). A first integration of eq. (3.6) gives

$$q \equiv \frac{dc''}{dz} = \mp\left[\frac{X}{2}(c''^4 - c''(0)^4) - \frac{2\Psi}{3}(c''^3 - c''(0)^3) + \Phi^2_{1st}(c''^2 - c''(0)^2) - 2(c'' - c''(0))\right]^{0.5}. \qquad 3.23$$

The internal effectiveness factor is given by Lee (1985) modified for this dimensionless problem where $D = L = 1$

$$\eta_{int} = \frac{\left(\dfrac{dc''}{dz}\right)_{z=1}}{r''_{Ps}} = \sqrt{-\frac{X}{2}c''(0)^4 + \frac{2\Psi}{3}c''(0)^3 - \Phi^2_{1st}c''(0)^2 + 2c''(0)} \qquad 3.24$$

since $r''_{Ps} = r''_P(z=1) = -1$. The negative root is required in eq. (3.23), since η_{int} is conventionally positive. Since $(dc''/dz)_{z=1}$ is negative and $c''(1) = 0$, c'' is positive within the slab for all monotonic concentration profiles.

The dimensionless reaction/diffusion expression, r''_P, is a cubic polynomial in c'', which, by the familiar Descartes' Rule of Signs (e.g. Borse, 1985), always has at

least one positive real root for $X \geq 0$ and $\Phi_{1st}^2 \geq 0$. The smallest positive root, labeled c''_{eq} and closest to $c''(z=1) = 0$, is needed to define the generalized, or normalized, Thiele modulus, Φ_G, which normalizes the asymptotic behavior of η_{int} such that $\eta_{int}\Phi_G \rightarrow 1$ at small η_{int}. It is given by

$$\Phi_G = \frac{1}{\sqrt{-\dfrac{X}{2}c''^4_{eq} + \dfrac{2\Psi}{3}c''^3_{eq} - \Phi_{1st}^2 c''^2_{eq} + 2c''_{eq}}} .$$

3.25

The generalized modulus can be determined without solving the governing differential equation. For irreversible reactions, c''_{eq} can be obtained by substituting zero for $\hat{c}_i$ in eq. (3.5) for each species involved in r_P, and then selecting the smallest (limiting reactant). For reversible reactions, $r''_P(c'')$ must be set equal to zero and solved for its roots by conventional methods.

To obtain concentration profiles, or $c''(0)$, eq. (3.23) must be integrated a second time. To facilitate this, first expand $q^2(c'')$ about $q^2(c''(0))$ in a Taylor series, noting that

$$\frac{d^n(q^2)}{dc''^n} = 0 \qquad n \geq 5$$

3.26

which yields the following revised polynomial expression for the rate

$$
\begin{aligned}
q^2 = \ & (2Xc''(0)^3 - 2\Psi c''(0)^2 + 2\Phi_{1st}^2 c''(0) - 2)(c'' - c''(0)) + \\
& (3Xc''(0)^2 - 2\Psi c''(0) + \Phi_{1st}^2)(c'' - c''(0))^2 + \\
& (2Xc''(0) - 2\Psi/3)(c'' - c''(0))^3 + \\
& (X/2)(c'' - c''(0))^4
\end{aligned}
\qquad 3.27
$$

and then define a new variable, σ, such that

$$
\begin{aligned}
c'' - c''(0) &\equiv \frac{(Xc''(0)^3 - \Psi c''(0)^2 + \Phi_{1st}^2 c''(0) - 1)/2}{\sigma - (3Xc''(0)^2 - 2\Psi c''(0) + \Phi_{1st}^2)/12} \\
&= \frac{6 r''_P (c'' = c''(0))}{12\sigma - (dr''_P/dc'')_{c''=c''(0)}} \, .
\end{aligned}
\qquad 3.28
$$

These substitutions convert the integration from z = 0 to z = z of eq. (3.23) into

$$
z = \int_{c''(0)}^{c''} \frac{dc''}{q} = \int_{\sigma}^{\infty} \frac{d\sigma}{\sqrt{4\sigma^3 - g_2\sigma - g_3}} \, .
\qquad 3.29
$$

The right-hand side of eq. (3.29) is recognized (Whittaker and Watson, 1950) as one definition of the Weierstrass elliptic Pe-function, $\wp$, such that $\sigma = \wp(z; g_2, g_3)$. The analytical solution is then given by

$$c''(z) = c''(0) + \frac{6r''_P(c'' = c''(0))}{12\wp(z;\, g_2,\, g_3) - (dr''_P/\, dc'')_{c''=c''(0)}} \qquad 3.30$$

or

$$c''(z) = c''(0) + \frac{6(Xc''(0)^3 - \Psi c''(0)^2 + \Phi_{1st}^2 c''(0) - 1)}{12\wp(z;\, g_2,\, g_3) - (3Xc''(0)^2 - 2\Psi c''(0) + \Phi_{1st}^2)} \qquad 3.31$$

subject to satisfying the remaining boundary condition, $c''(1) = 0$, to evaluate the still undetermined midplane concentration, $c''(0)$. The two parameters, g_2 and g_3, are the invariants of $q^2(c'')$ and its permutations, given by

$$g_2 = \frac{X}{2}\left[-\frac{X}{2}c''(0)^4 + \frac{2\Psi}{3}c''(0)^3 - \Phi_{1st}^2 c''(0)^2 + 2c''(0) \right] - \frac{\Psi}{3} + \frac{\Phi_{1st}^4}{12} \qquad 3.32$$

$$g_3 = \left[\frac{3X\Phi_{1st}^2 - \Psi^2}{36} \right]\left[-\frac{X}{2}c''(0)^4 + \frac{2\Psi}{3}c''(0)^3 - \Phi_{1st}^2 c''(0)^2 + 2c''(0) \right] \qquad 3.33$$
$$+ \frac{\Phi_{1st}^2\Psi}{36} - \frac{\Phi_{1st}^6}{216} - \frac{X}{8}$$

and the bracketed term in common to g_2 and g_3 is η_{int}^2. The two invariants reduce to those for second-order reversible reaction systems when X is zero. Invariant g_2 is zero on $(X = 0,\ \Psi = \Phi_{1st}^4/4,\ \Phi_{1st}^2)$, while g_3 is zero on $(X = \Phi_{1st}^6/27,\ \Psi = \Phi_{1st}^4/3,\ \Phi_{1st}^2)$. These two curves are on the boundary of the parameter space for conventional reversible or irreversible reaction systems discussed below. Numerically, $g_2 > 0$ and $g_3 < 0$ away

from these two curves for the third-order reaction systems discussed here, except possibly in a narrow region near the parameter space boundary and between these two curves (perhaps round-off error). Generally, the expansion for $\wp$ contains positive and negative terms for third-order systems.

The analytical solution is completed by evaluating the remaining free parameter in the equation, $c''(0)$, which must be chosen to satisfy the remaining boundary condition, $c''(1) = 0$. This requires solution of an implicit nonlinear transcendental equation, eq. (3.31), since g_2 and g_3 are also expressed in terms of $c''(0)$. Starting guesses are often required for numerical solution of such equations. The behavior of the dimensionless midplane concentration, $c''(0)$, is much the same as it was in Chapter Two for second-order reactions, i.e. bound above by one-half and c''_{eq} and below by zero. Finally, note the first-order problem, $d^2c''/dz^2 = \Phi_{1st}^2 c''^2 - 1$, solution is $c''(0) = (1 - 1/\cosh\Phi_G)/\Phi_G^2$, where $\Phi_G = \Phi_{1st}$ for first-order reactions, but is given by eq. (3.25) above for third-order.

Figure 3.1 plots $c''(0)$ versus Φ_G for various cases of second-order and third-order reaction and diffusion systems. (The curves for $\Psi = \Phi_{1st}^2 = 0$ and for $X = \Phi_{1st}^2 = 0$ are special limiting cases that will be discussed later.) The first-order assumption gives a reasonable guess, especially for irreversible reactions, rather than a bound, for $c''(0)$. For $\Phi_G > 5$, c''_{eq} is a better guess in many cases than the first-order guess and is almost as good as $c''(0)$ in determining the internal effectiveness factor. The first-order guess is the best of the three from $0.2 < \Phi_G < 3$. The 20% deviations from first-
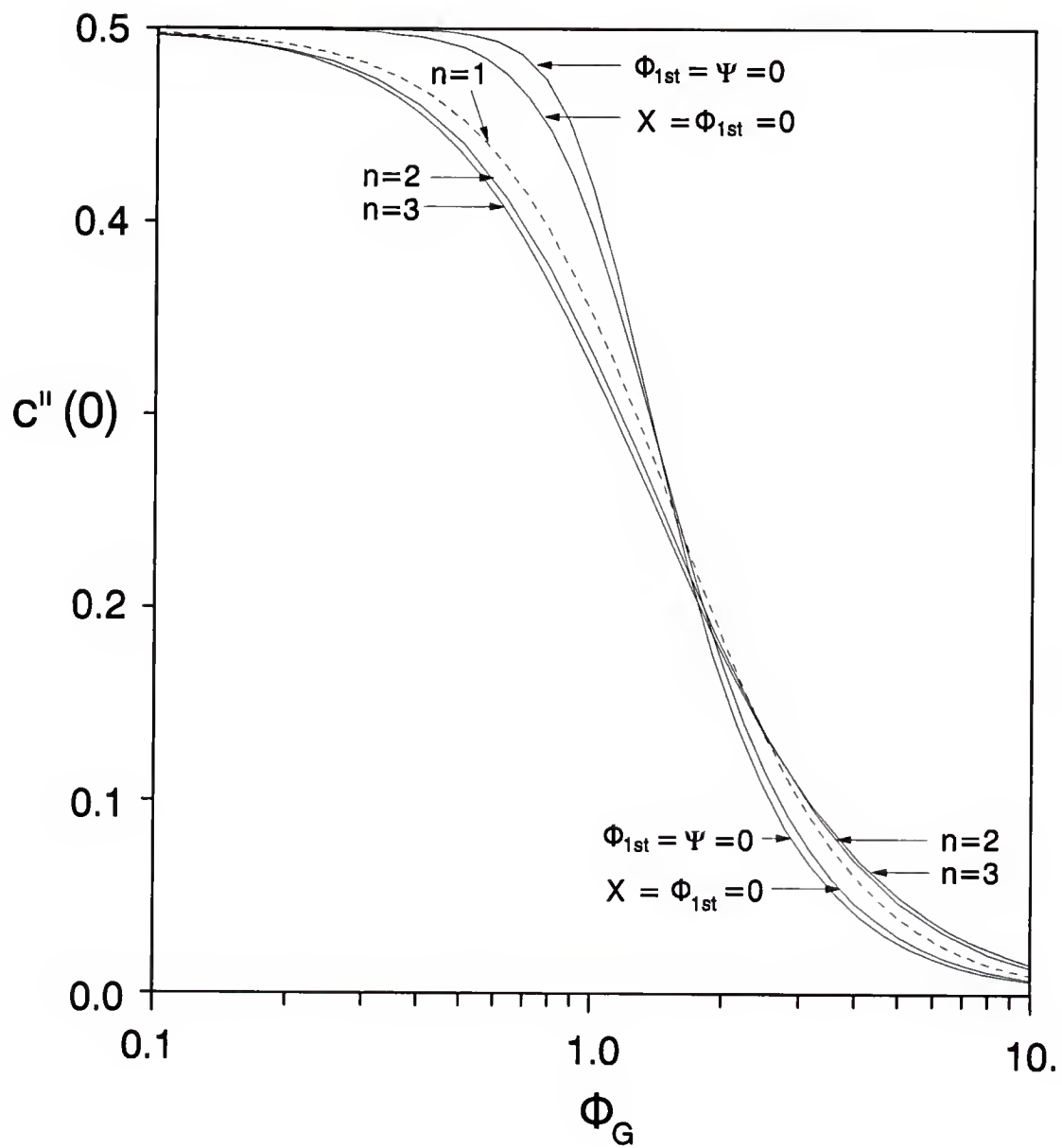
Figure 3.1 The Dimensionless Midplane Concentration for Selected Special Cases.

order behavior in Figure 3.1 show some of the justification for pursuing an analytical solution to the higher order reaction and diffusion problem.

There is one restriction on the solution in eq. (3.31), namely that $g_2^3 \neq 27g_3^2$. When this equality occurs, the square root argument of eq. (3.23) has a repeated root and can be integrated by conventional methods. In these cases a simpler expression than the full definition of $\wp(z; g_2, g_3)$ can be used in evaluating eq. (3.31). For our purposes, one case is primarily important. When $g_2^3 = 27g_3^2$, $g_2 > 0$, and $g_3 < 0$, then

$$\alpha = \sqrt{\frac{g_2}{12}} = \sqrt[3]{\frac{-g_3}{8}}$$

$$\wp(z: 12\alpha^2, -8\alpha^3) = \alpha + \frac{3\alpha}{\sinh^2(\sqrt{3\alpha}\, z)}.$$

3.34

As the magnitude of the three moduli increase, g_2 and g_3 increase in magnitude in general. Round-off error can then obscure whether $g_2^3 = 27g_3^2$ is satisfied, but the above limiting case equation for $\wp$ is an extremely good approximation under these conditions regardless of whether $g_2^3 = 27g_3^2$ holds exactly.

Restrictions on the Feasible Parameter Space

Given the analytical solution derived in eq. (3.31), where should it be applied in (X, Ψ, Φ_{1st}^2) space to study third-order irreversible and reversible reactions of the types listed in Table 3.1? Restrictions tighter than the obvious ($X \geq 0$, $\Phi_{1st}^2 \geq 0$) apply to the parameters. Before exploring these, some notational bookkeeping is useful. Let:

$$\Phi_{ijk}^2 = L^2 k_i \hat{c}_{is} \hat{c}_{js} / D_k \qquad \Phi_{i+j}^2 = L^2 k_i \hat{c}_{is} / D_j$$

$$\Phi_i^2 = L^2 k_i / D_i \qquad \Gamma_{lm} = D_l \hat{c}_{ls} / D_m \hat{c}_{ms}$$

3.35

where k_i is the rate constant associated with $\hat{c}_i$, and the i,j,k are either all reactants or all products, while l,m are one reactant and one product. The Φ above are the same as those introduced in Chapter Two plus Φ_{ijk}^2. This new irreversible reaction Thiele modulus arises naturally in making common third-order irreversible reactions dimensionless. The three parameters, X, Ψ, Φ_{1st}^2, can all be expressed in terms of a single Γ (no Γ required for irreversible reactions) and as few Φ as there are species (including one if the reverse reaction is zeroth-order). With over 20 third-order systems to study, a tabulation of moduli expansions was not done as for the second-order cases. General expressions exist for X, Ψ, and Φ_{1st}^2 as shown above. Several cases will be considered below, however, in finding bounds for the parameter space. Consider the three possible third-order irreversible elementary reactions first:

Case 21, Table 3.1:   3A $\rightarrow$ products

$$\Phi_{1st,f}^2 = 9 \Phi_{AAA}^2$$
$$\Psi_f = 27 \Phi_{AAA}^4 = \Phi_{1st,f}^4 / 3$$
$$X_f = 27 \Phi_{AAA}^6 = \Phi_{1st,f}^6 / 27$$

3.36

Case 20, Table 3.1:   2A + B $\rightarrow$ products

$$\Phi_{1st,f}^2 = 4 \Phi_{ABA}^2 + \Phi_{AAB}^2$$
$$\Psi_f = 4 \Phi_{ABA}^2 (\Phi_{ABA}^2 + \Phi_{AAB}^2)$$
$$X_f = 4 \Phi_{ABA}^4 \Phi_{AAB}^2$$

3.37

Case 19, Table 3.1: $A + B + C \rightarrow$ products

$$\Phi_{1st,f}^2 = \Phi_{ABC}^2 + \Phi_{BCA}^2 + \Phi_{CAB}^2$$
$$\Psi_f = \Phi_{ABC}^2 \Phi_{CAB}^2 + \Phi_{ABC}^2 \Phi_{BCA}^2 + \Phi_{CAB}^2 \Phi_{BCA}^2 \qquad 3.38$$
$$X_f = \Phi_{ABC}^2 \Phi_{BCA}^2 \Phi_{CAB}^2$$

where the subscript, f, denotes a forward reaction. One can solve the problem:

maximize Ψ_f subject to fixed $\Phi_{1st,f}^2$ and non-negative Φ_{ijk}^2. Case 21 is moot. Cases 19 and

20, however, give an identical result to case 21: $\Psi_{max,f} = \Phi_{1st}^4/3$, at $\Phi_{ABC}^2 = \Phi_{BCA}^2 = \Phi_{CAB}^2$

$= 2\Phi_{ABA}^2 = \Phi_{AAB}^2 = 3\Phi_{AAA}^2 = \Phi_{1st}^2/3$. X_f has the same (maximum) value, $\Phi_{1st}^6/27$, for all

three cases as well in this special case. The result that $\Psi \leq \Phi_{1st}^4/3$ applies equally to the

reverse reaction in the absence of the forward reaction ($\Phi_{1st,r}^2$, Ψ_r, X_r). To extend this to

reversible reactions note that $\Phi_{1st}^2 = \Phi_{1st,f}^2 + \Phi_{1st,r}^2$, see eq. (3.10). The modulus, Ψ, can

be written as $\Psi = \Psi_f + \Psi_r$ - (other nonnegative cross terms), if eq. (3.9) is expanded

and terms in k_f^2, k_r^2 and $k_f k_r$ are collected. Then

$$\frac{\Phi_{1st}^4}{3} \geq \frac{\Phi_{1st,f}^4}{3} + \frac{\Phi_{1st,r}^4}{3} \geq \Psi_f + \Psi_r \geq \Psi . \qquad 3.39$$

Thus, $\Psi \leq \Phi_{1st}^4/3$ in general. A similar argument is inconclusive applied to X.

Are there also general restrictions on X? Certainly there are for irreversible

reactions which must be confined to the region of three real roots of r''$_p$. There is a

real root for each species in the irreversible third-order reaction with multiplicity equal

to the stoichiometric coefficient. A surface exists in (X, Ψ, Φ_{1st}^2) space which divides the

parameter space into regions with one or three real roots, while cases with multiple real

roots (double or triple) lie on the surface itself. The surface of multiple roots is most conveniently given by

$$X_m = \frac{9\,\Phi_{1st}^2\Psi \;-\; 2\,\Phi_{1st}^6 \;\pm\; 2\sqrt{(\Phi_{1st}^4 - 3\Psi)^3}}{27} \qquad\qquad 3.40$$

where m denotes the surface of multiplicity. With $\Phi_{1st}^2 \geq 0$ and the positive root in eq. (3.40), $X_{m+} \geq 0$ for all $\Psi \leq \Phi_{1st}^4/3$. However, the negative root of eq. (3.40) and $\Phi_{1st}^2 \geq 0$ only allows $X_{m-} \geq 0$ on $\Phi_{1st}^4/4 \leq \Psi \leq \Phi_{1st}^4/3$. The smaller of these range limits, $\Phi_{1st}^4/4$, is the upper bound on Ψ for second-order reversible reaction systems ($X = 0$, Chapter Two). Figure 3.2 gives a typical cross-section of X-Ψ space at $\Phi_{1st}^2 = 3$. The space is subdivided by curves delineating between regions with one or three real roots of $r''_P(c'')$. Furthermore, Ψ is always nonnegative for irreversible reactions. Although irreversible reactions of second-order or third-order lie exclusively in the cross-hatched region, reversible reactions are not excluded from this region and extend the parameter space considerably beyond to regions of negative Ψ and $X > X_{m+}$. Reversible reactions are not required to have three real roots, although the forward or reverse reaction individually, and exclusive of the other, could have up to three real roots depending on its order.

Reversible reactions may, however, be unable to extend the parameter space to the wedge shaped region, $0 \leq X < X_{m-}$, located above $\Phi_{1st}^4/4 \leq \Psi \leq \Phi_{1st}^4/3$, even though this region contains a positive c''_{eq} and satisfies $\Psi \leq \Phi_{1st}^4/3$ (for second-order
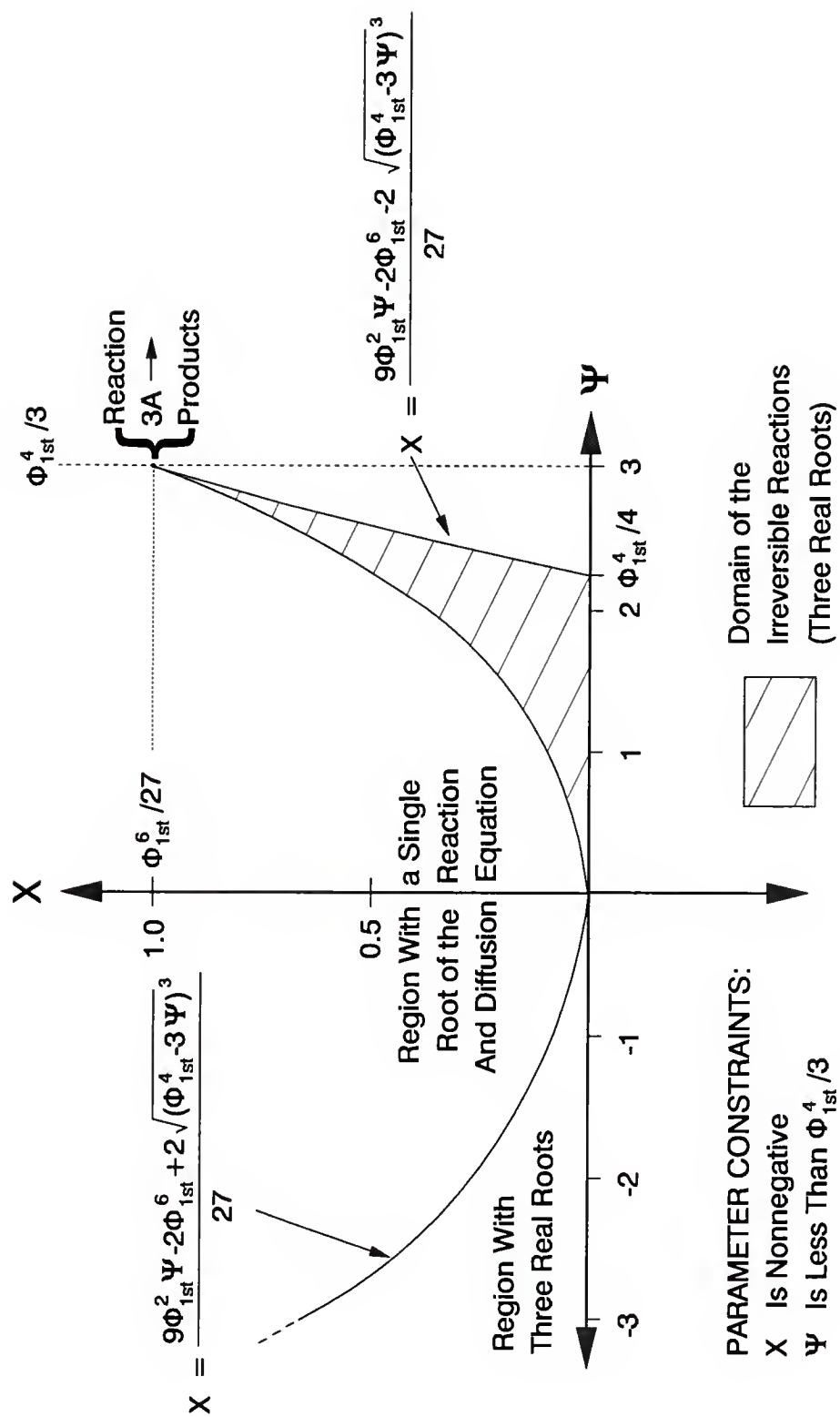
Figure 3.2 Typical Cross-Section of X-Ψ-Φ_{1st}^2 Parameter Space for $\Phi_{1st}^2 = 3$.

systems, c''_{eq} became a complex number corresponding to an inconsistency with the original physical properties of the problem). The surface for X_{m-} does give rise to a discontinuity in c''_{eq}, the smallest positive root of the reaction and diffusion equation. The single root case's c''_{eq} is continuous with the <u>largest</u> of the three positive real roots across this boundary, rather than the smallest. In the transition from $X < X_{m+}$ to $X > X_{m+}$, the single root case's c''_{eq} is continuous with the <u>smallest</u> root ($= c''_{eq}$) from the three positive root region. This transition was verified as allowable by testing reversible third-order reaction systems. We have adopted as a supposition (unproven) that the wedge shaped region bounded by the surfaces: $\Psi = \Phi_{1st}^4/3$, $X = 0$, and $X = X_{m-}$, is outside of the feasible parameter space for third-order reversible and irreversible reactions. One argument for this involves not having an abrupt transition from feasible to infeasible parameter space as $X \to 0$ along $\Phi_{1st}^4/4 \le \Psi \le \Phi_{1st}^4/3$. Another argument involves the belief that c''_{eq} should be a continuous variable in the feasible parameter space. There may be additional parameter space constraints not yet discovered.

The constraints on the parameter space for third-order reversible and irreversible reaction systems can be summarized as

$$\Phi_{1st}^2 \ge 0$$
$$\Psi \le \Phi_{1st}^4/3$$
$$X \ge 0 \qquad\qquad\qquad 3.41$$
$$X \ge \frac{9\Phi_{1st}^2\Psi - 2\Phi_{1st}^6 - 2\sqrt{(\Phi_{1st}^4 - 3\Psi)^3}}{27}$$

where the fourth condition is tentative, but only applies on

$$\frac{\Phi_{1st}^4}{4} \leq \Psi \leq \frac{\Phi_{1st}^4}{3} \qquad\qquad 3.42$$

since its right-hand-side expression becomes negative for smaller Ψ, and the third condition supersedes the fourth.

Internal Effectiveness Factors of Third-Order Reactions

Perhaps the single most important result that can be calculated from the analytical solution is the internal effectiveness factor, eq. (3.24). The behavior of characteristic properties, such as the internal effectiveness factor, η_{int}, or the dimensionless midplane concentration, c''(0), can be investigated now that the parameter space boundary for reversible third-order reactions has been identified. In Chapter Two both of the above properties were studied as functions of the two parameters, Φ_{1st}^2 and Ψ for second-order systems. It could seen there that η_{int} and c''(0) are strongly correlated as eq. (3.24) suggests. Therefore general graphical results will only be presented for η_{int} as a function of (X, Ψ, Φ_{1st}^2), because of the increased burden of a third parameter.

Unless the three parameters are directly interrelated, such as in eq. (3.36) for Case 21 of Table 3.1, a given third-order kinetic scheme gives rise to a bounded region rather than a smooth curve on a plot of η_{int} versus the generalized Thiele modulus, Φ_G. Nonetheless, six significant special cases, described in Table 3.2 below and calculated using eq. (3.31) except when r''$_p$ was lower than second-order, are presented in Figure 3.3.
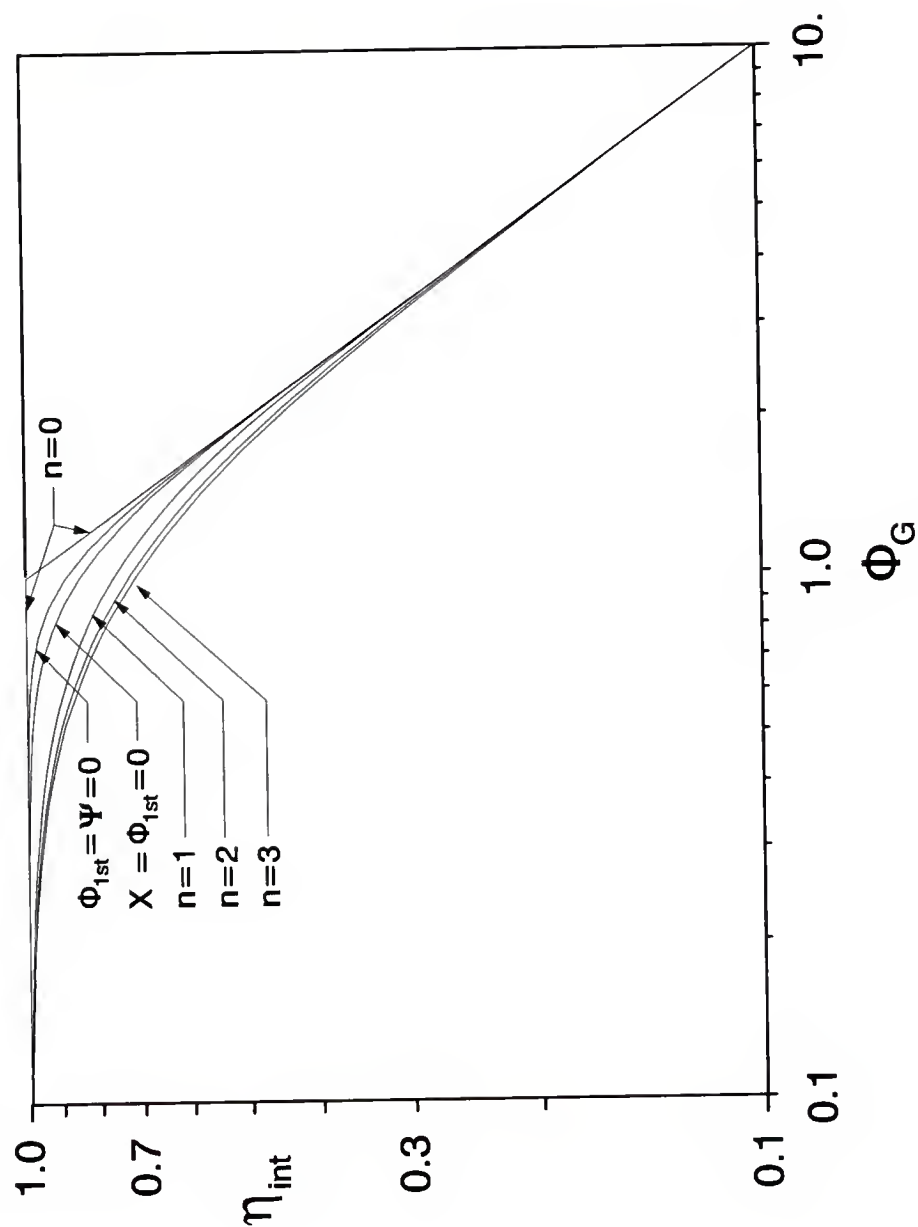
Figure 3.3 Limiting Cases for Small Integer Polynomial Kinetic Rate Expressions for Simultaneous Reaction and Diffusion in a Slab.

Table 3.2. Parameter Summary of Six Special Cases Presented in Figure 3.3.

	$\underline{1}$	$\underline{2}$	$\underline{3}$	$\underline{4}$	$\underline{5}$	$\underline{6}$
X:	0	0	0	$\Phi_{1st}^6/27$	X	0
Ψ:	0	0	$\Phi_{1st}^4/4$	$\Phi_{1st}^4/3$	0	Ψ
Φ_{1st}^2:	0	Φ_{1st}^2	Φ_{1st}^2	Φ_{1st}^2	0	0
Φ_G:	$kL^2/2D\hat{c}_s$	Φ_{1st}^2	$3\Phi_{1st}^2/4$	$2\Phi_{1st}^2/3$	$(8X/27)^{1/6}$	$(-9\Psi/16)^{1/4}$

Columns 1-4 correspond to nth-order power law kinetics, $v_i r_P = k\hat{c}^n$ with n = 0, 1, 2, and 3, respectively. This information has been previously published by Bischoff (1965), but perhaps not with the benefit of analytical solutions for second-order or third-order solutions. The curve for n = 3, 3A → products, bounds third-order reaction results from below, while the curve for n = 2 bounds second-order reaction results from below. Irreversible second-order and third-order reactions are asymptotically bounded above by the curve for n = 1. The curve from column 5 seems to asymptotically bound third-order reversible reaction results from above, while the curve from column 6 performs the same function for second-order reversible reaction results. (These last two cases are purely hypothetical, since $\Phi_{1st}^2 = 0$ implies $\Psi = 0$ and X = 0, but computed results for allowed parameter values approach these curves quite closely. Ψ is strictly negative in case 6.) The curve for n = 0 bounds all positive order results from above, (Aris, 1975).

A second third-order system can be described by fewer than three parameters. This is the irreversible reaction, 2A + B → products. As seen in eq. (3.37) the three

third-order parameters, X, Ψ, and Φ^2_{1st}, can be expressed in terms of two species parameters

$$\Phi^2_{ABA} \equiv \frac{L^2 k_f \hat{c}_{As} \hat{c}_{Bs}}{D_A} \qquad \Phi^2_{AAB} \equiv \frac{L^2 k_f \hat{c}_{As}^2}{D_B}. \qquad 3.43$$

Three views of the surface of η_{int} versus Φ^2_{ABA} and Φ^2_{AAB} are shown in Figure 3.4. When Φ^2_{AAB} is small relative to Φ^2_{ABA}, the solution is asymptotic to that for the second-order irreversible reaction, $2A \rightarrow$ products, with a pseudo rate constant, $k_f\hat{c}_{Bs}$; see the lower left of Figure 3.4. When Φ^2_{ABA} is small relative to Φ^2_{AAB}, the solution is asymptotic to that for the first-order reaction, $B \rightarrow$ products, with pseudo rate constant, $k_f\hat{c}_{As}^2$; see the lower right of Figure 3.4. The plane at $\Phi^2_{ABA} = 0.0025$ is a virtually first-order region with differences between η_{int} and $\tanh(\Phi_{AAB})/\Phi_{AAB}$ being less than 0.1%. When $2\Phi^2_{ABA} = \Phi^2_{AAB}$, the solution corresponds to that for the irreversible third-order reaction, $3A \rightarrow$ products. Because species A appears twice in the rate expression, it gives rise to a repeated root in r''$_P$, and the parameter space is interrelated through the relationship describing the surface of repeated roots

$$X = \frac{9\Phi^2_{1st}\Psi - 2\Phi^6_{1st} \pm 2\sqrt{(\Phi^4_{1st} - 3\Psi)^3}}{27} \qquad 3.44$$

which is another way of saying that there are in reality only two parameters for this case.

In Figure 3.2, the reaction, $2A + B \rightarrow$ products, lies along the boundary of the cross-hatched region. In this figure, $\Phi^2_{1st} = 3$, and as $4\Phi^2_{ABA}$ goes from three to zero,
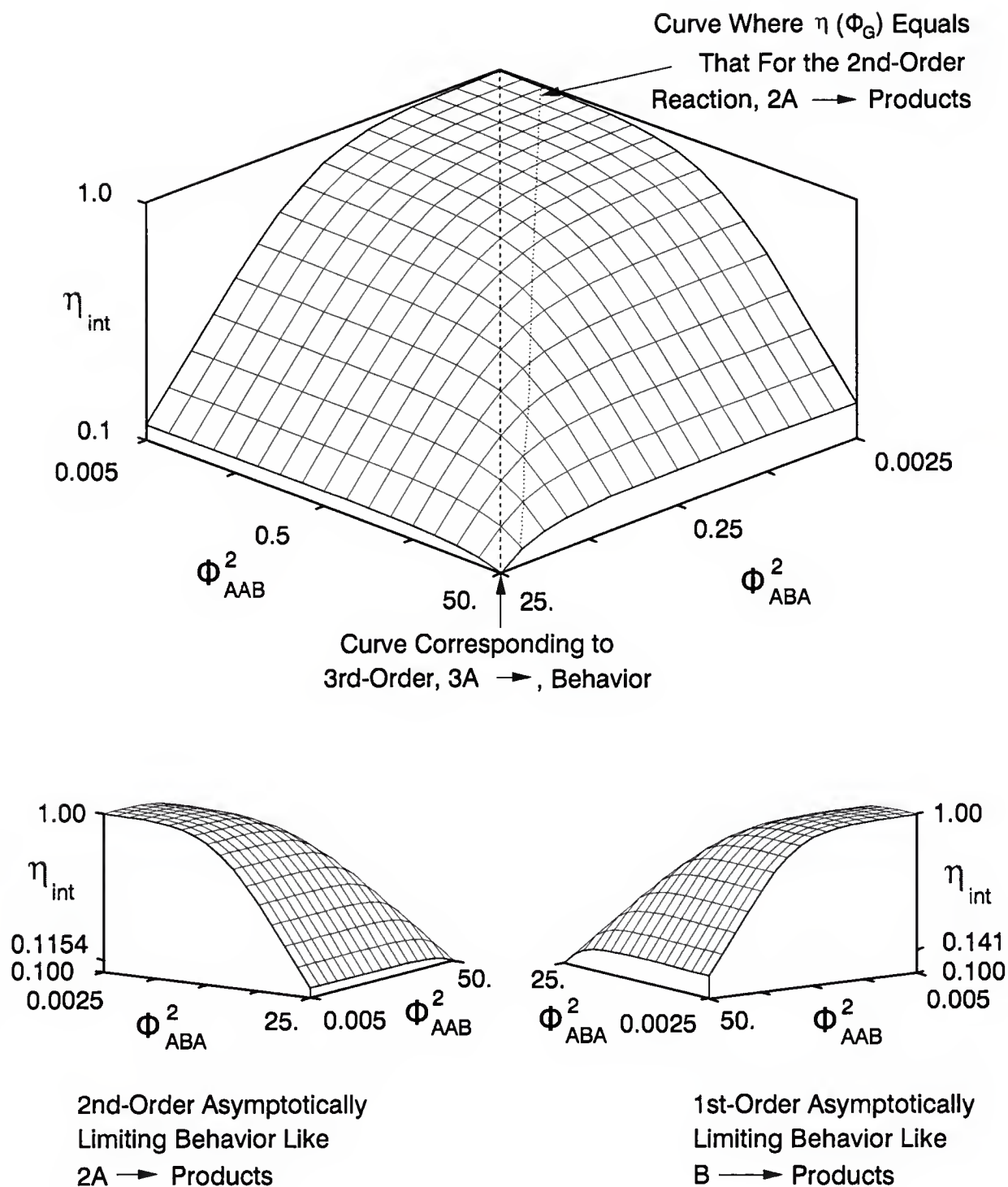
Figure 3.4 The Internal Effectiveness Factor for the Irreversible Third-Order Reaction $2A + B \to$ Products As a Function of the Two Species' Moduli.

Φ_{AAB}^2 must go from zero to three to keep Φ_{1st}^2 constant. The reaction tracks around the cross-hatched boundary from (X = 0, Ψ = 9/4); to the point of n = 3 power law kinetics (X = 1, Ψ = 3) when $2\Phi_{ABA}^2 = \Phi_{AAB}^2 = 1$; to (X = 0, Ψ = 0). As the parameter path takes the reaction from n = 3 power law kinetics to n = 1 power law kinetics (upper boundary), η_{int} would be expected to pass through n = 2 power law kinetic behavior based on the relative position of these curves on a plot of η_{int} versus Φ_G, such as Figure 3.3. This transition is also marked in Figure 3.4, just to the right of the n = 3 power law behavior as $\eta(\Phi_G)$ equals that for 2A → products. Consequently, nearly half of the parameter region shown has η_{int} values that would lie above the curve for n = 2 power law kinetics if plotted in Figure 3.3.

For an irreversible reaction with three species instead of two, the dominance of any single species' moduli, Φ_{ijk}^2, leads to nearly first-order behavior as described for species B above. Third-order power law behavior only occurs when all three species' moduli are equal. Second-order power law behavior would be observed if two species' moduli were equal and dominant. Other cases fall in between the three power law curves.

Reversible reactions lead to results that can lie well outside the limits of first-order to third-order power law behavior in Figure 3.3, due to diffusive enhancement effects on the product side. Figures 3.5 through 3.9 give ten surfaces of η_{int} versus X and Φ_{1st}^2 at selected values of Ψ. The ten surfaces were developed with equivalent perspectives and relative axis scaling. The range in X, from $3.375*10^{-6}$ to $3.375*10^{+6}$, was deliberately chosen for its similar influence on η_{int} compared to a range in Φ_{1st}^2 from
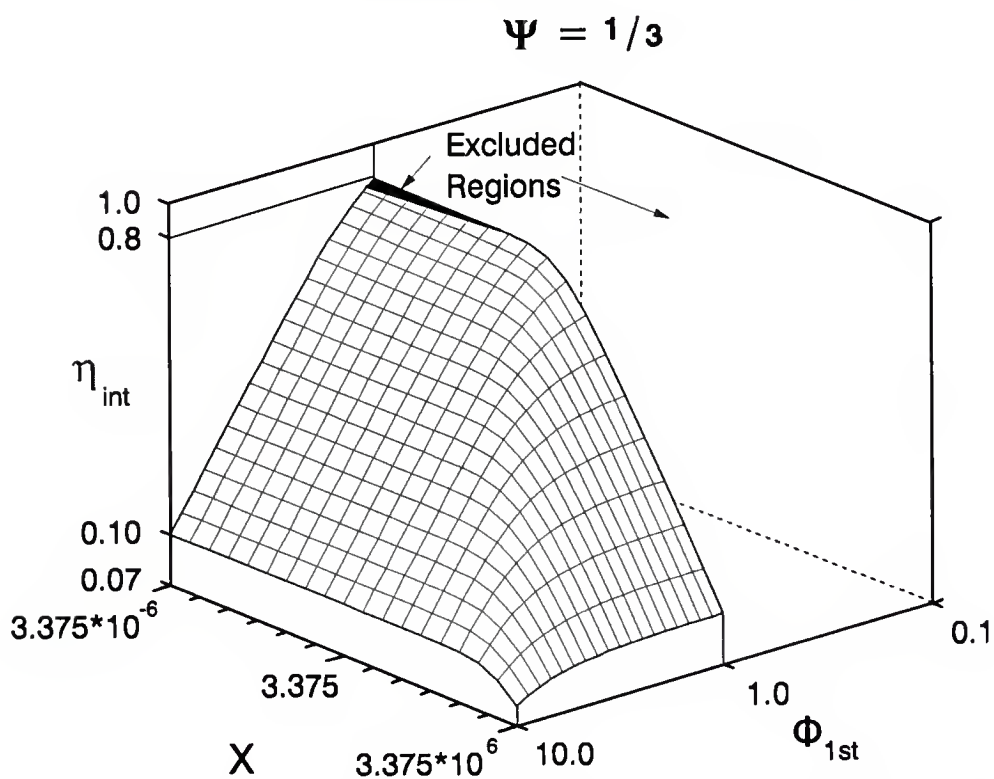
$\Psi = 1/300$

$\Psi = 1/3$

Figure 3.5 Values of the Internal Effectiveness Factor for General Third-Order Reaction Systems for Positive Values of the Second-Order Modulus, Ψ.
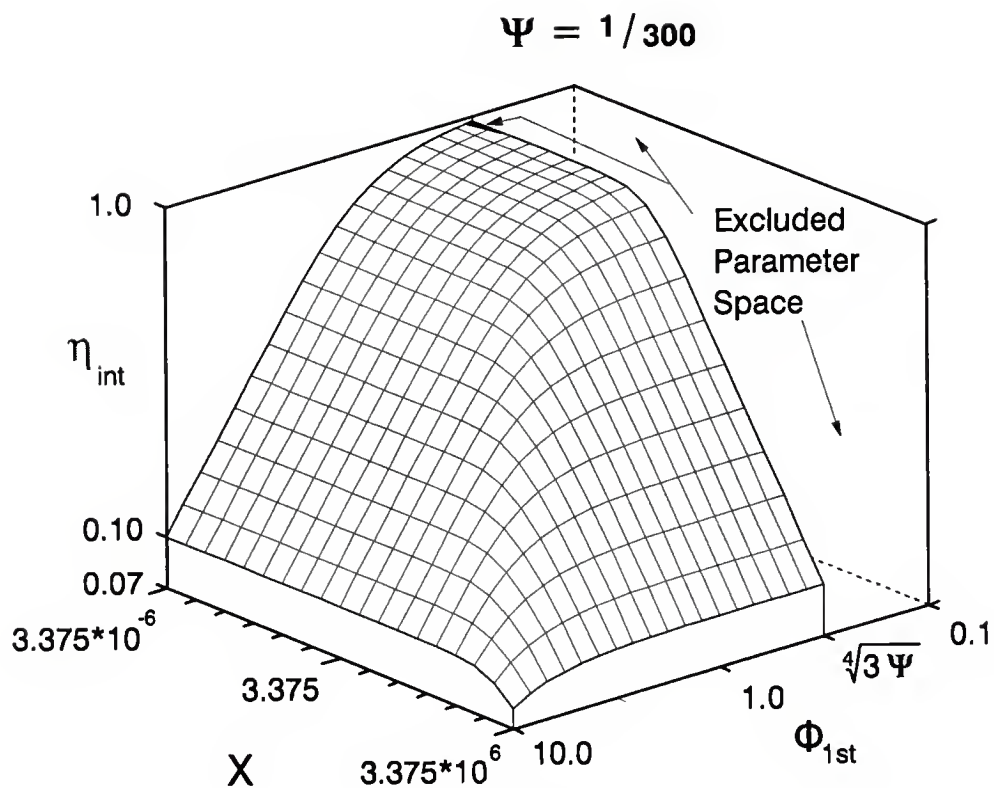
$$\Psi \ = 3\,^{1}/_{3}$$

$$\Psi \ = 33\,^{1}/_{3}$$
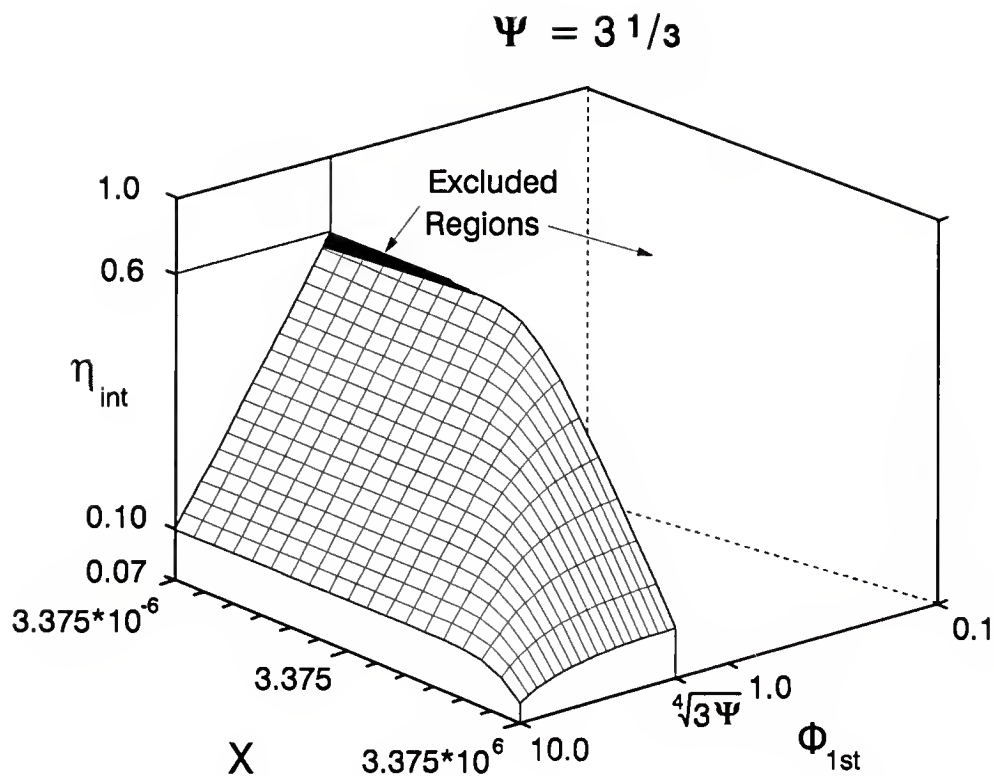
Figure 3.6 Values of the Internal Effectiveness Factor for General Third-Order Reaction Systems for Positive Values of the Second-Order Modulus, Ψ.
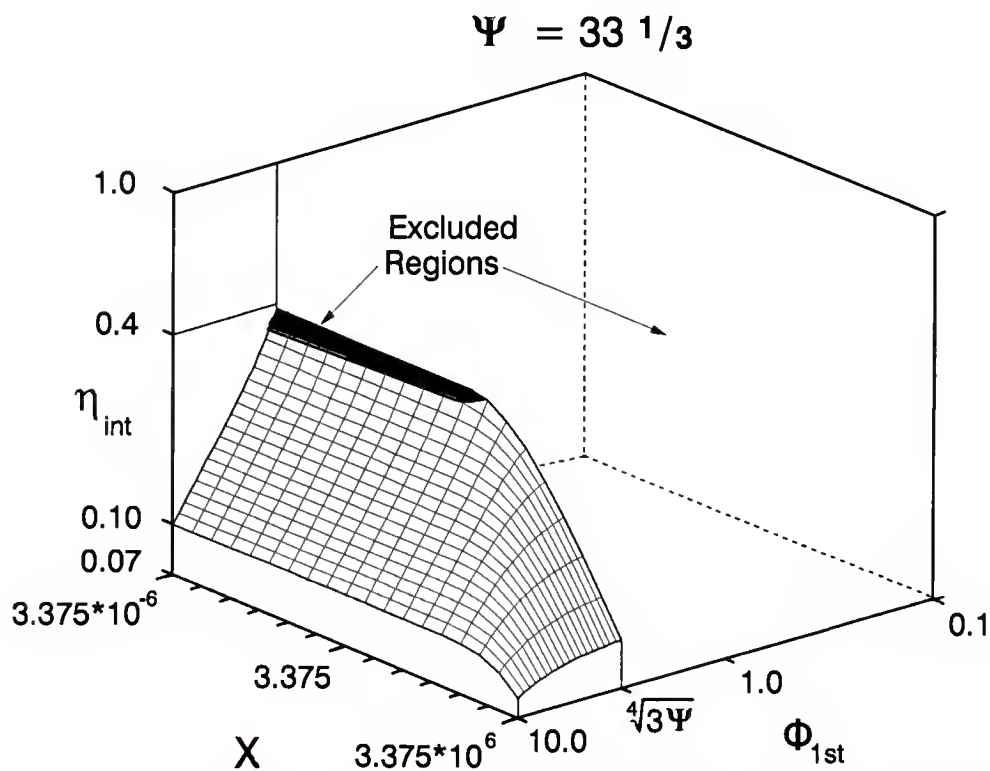
Figure 3.7 Values of the Internal Effectiveness Factor for General Third-Order Reaction Systems for Values of the Second-Order Modulus, Ψ, of zero and -1.

Figure 3.8 Values of the Internal Effectiveness Factor for General Third-Order Reaction Systems for Negative Values of the Second-Order Modulus, Ψ.

Figure 3.9 Values of the Internal Effectiveness Factor for General Third-Order Reaction Systems for Negative Values of the Second-Order Modulus, Ψ.
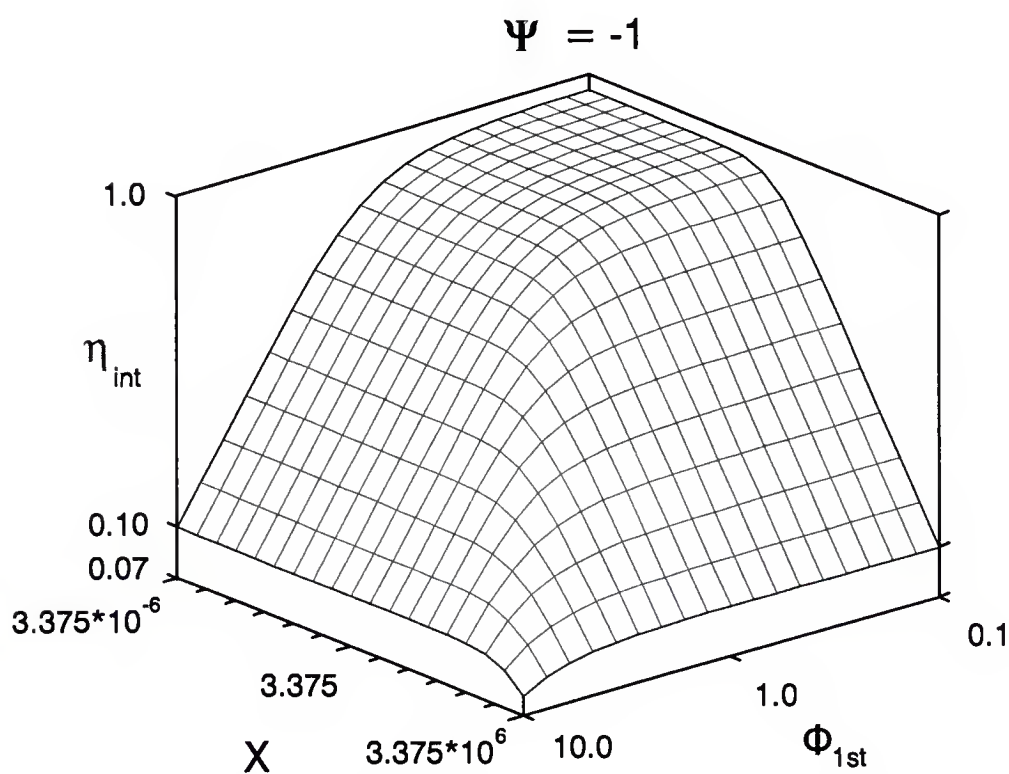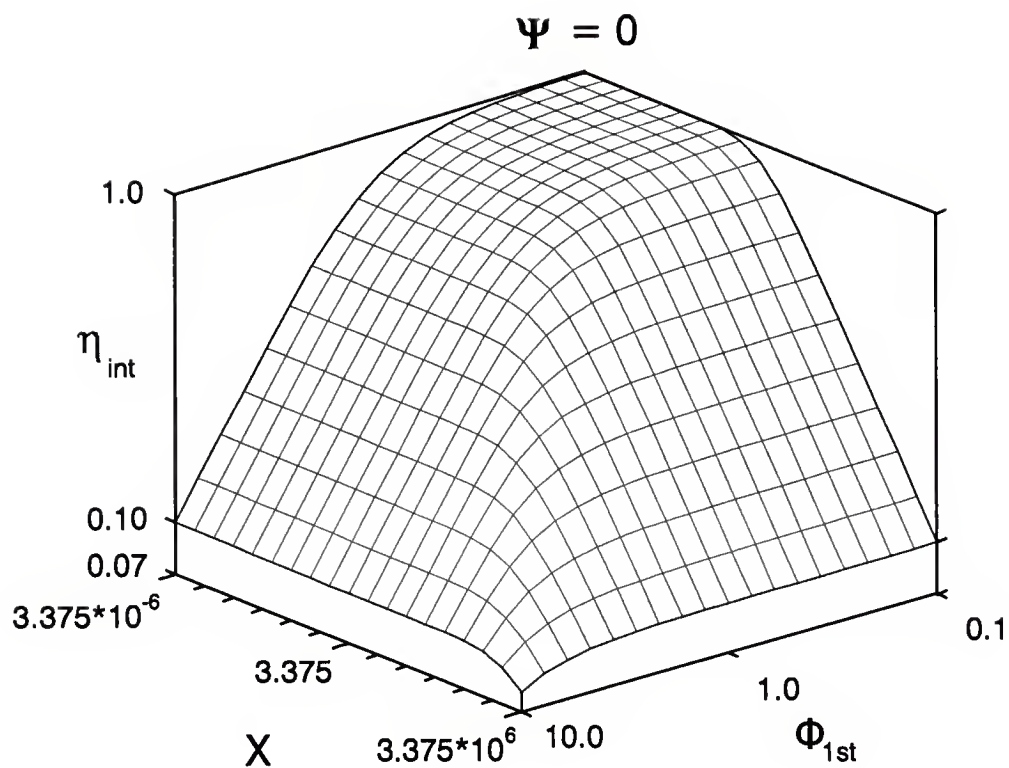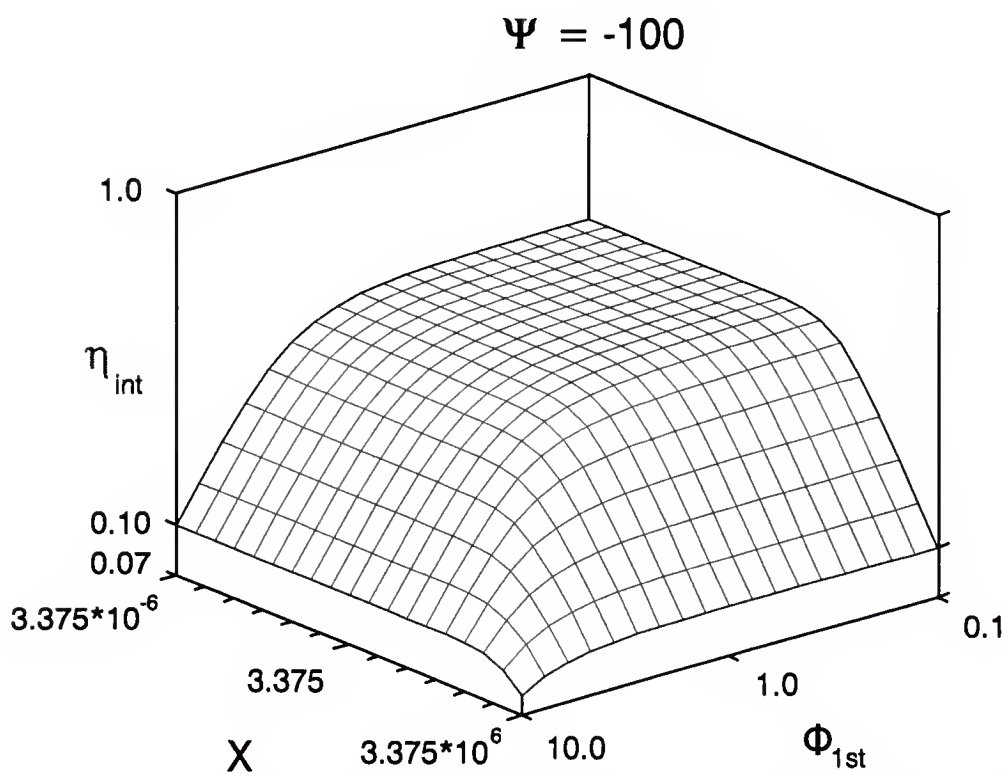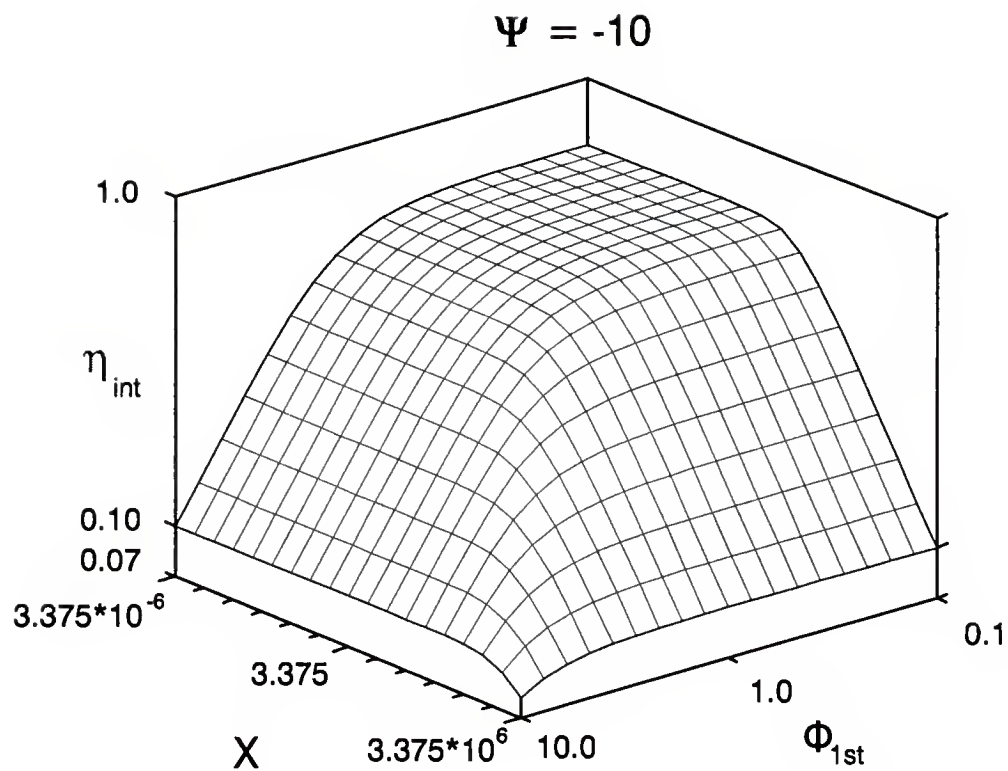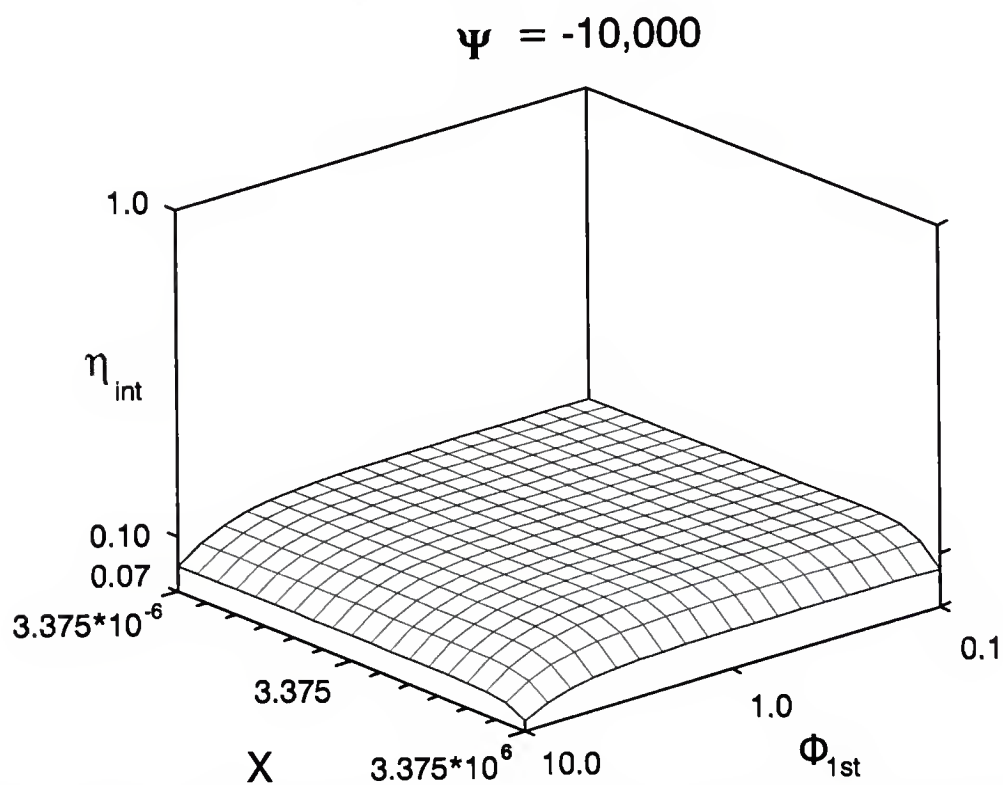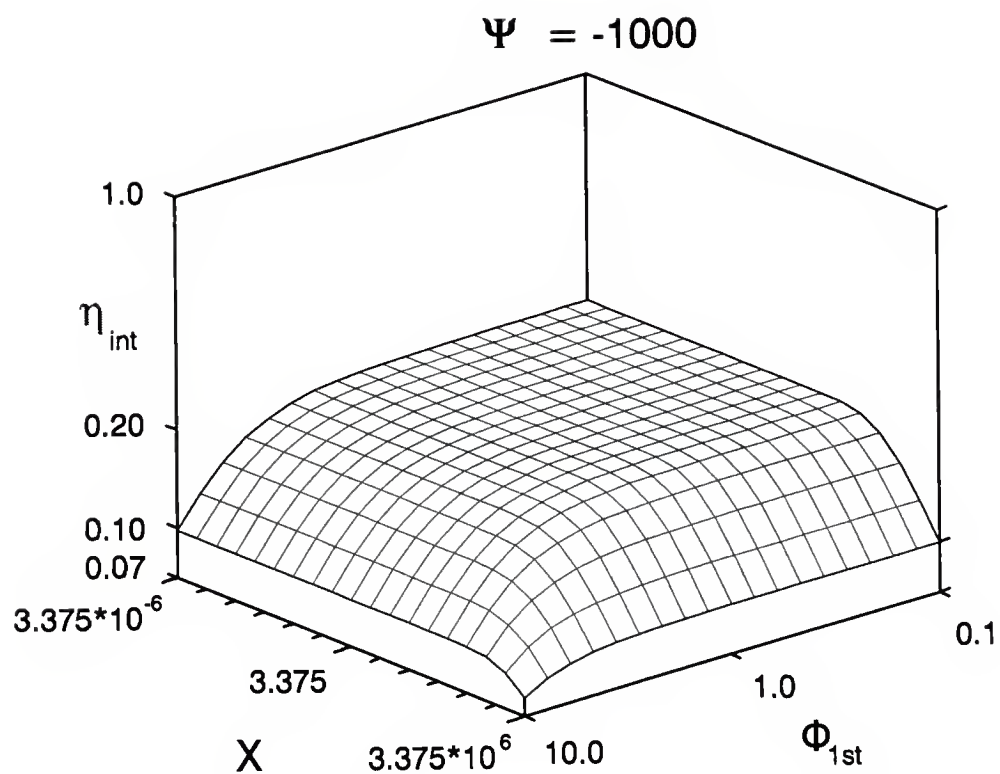
0.01 to 100. Both ranges are comparable to a range of 0.1 to 10 for Φ_G. The comparable range for Ψ is from $-1.77778*10^{-4}$ to $-1.77778*10^{+4}$. Thus the conventional semi-quantitative criterion for the transition from approximately diffusion free behavior to strongly diffusion limited behavior as Φ_G goes from 0.3 to 3.0 can be rescaled for each modulus, i.e. as Φ_{1st} goes from 0.3 to 3.0, as $-\Psi$ goes from 0.0144 to 144, and as X goes from 0.00246 to 2460. Only one modulus needs to exceed the $\Phi_G = 3$ criterion for strongly diffusion limited behavior, while all three moduli must be comparably less than $\Phi_G = 0.3$ to approach the diffusion free region. The hypothetically invalid wedge shaped region in the parameter space is marked on Figures 3.5 and 3.6, where it is seen to be a comparatively minor fraction of the total solution surface.

It can be seen in the surfaces for nonpositive Ψ, Figures 3.7 to 3.9, that the transition between asymptotes is very abrupt (i.e. nearly an acute angle) along a line of small Φ_{1st}^2, while the transition is more gradual along a line of constant and small X. When the solution points used to generate the surfaces for nonpositive Ψ were plotted on the coordinates of Figure 3.3, (Φ_G, η_{int}), all points were found to lie above the curve for n = 1 power law behavior. The data at small Φ_{1st}^2 lie near the curve for $\Phi_{1st}^2 = \Psi = 0$, which in turn lies near the curve for zeroth-order kinetics, which has an acute angle discontinuity at $\Phi_G = 1$. A similar phenomenon, but with a more gradual tranisition, was observed in second-order reversible reaction systems, where the case $\Psi = 0$ corresponded exactly to first-order behavior, and results of calculations with negative Ψ fell between the curves for n = 1 power law behavior and the curve for $X = \Phi_{1st}^2 = 0$ in Figure 3.3. For third-order reversible reaction systems in general, the data fall

between curves for n = 3 power law behavior and the curve for $\Psi = \Phi_{1st}^2 = 0$ in Figure 3.3. The clear conclusion is that third-order reversible reaction behavior encompasses second-order reversible reaction behavior and adds new possibilities. However, for third-order reactions in general, the dividing line between results above or below the n = 1 power law kinetic curve is not $\Psi = 0$, but lies on the positive Ψ side of this plane for nonzero X. Determining the criterion for the transition through first-order behavior as a function of the three moduli is an area for possible future study.

Of the three parameters, Ψ may be the most susceptible to selective adjustment. While all three parameters are subject to various powers of L, k_f and/or k_r, D_i and $\hat{c}_{is}$, the lead term in Ψ, see eq. (3.12), can be adjusted to some fairly arbitrary value, because it contains products of differences of positive terms (for reversible reactions). The other two moduli may remain nearly constant during such adjustment. Thus a range of optimization problems is developed, i.e. maximize $\eta_{int}r_{Ps}$ subject to reasonable constraints. Being diffusion limited through Ψ alone may frequently be avoidable.

Concluding Remarks

The development of a unifying three-parameter basis and an analytical solution for third-order reversible reaction and diffusion in an isothermal slab increases the available number of theoretical models for such processes. The broad range of η_{int} behavior at constant Φ_G is a suitable caution against broadly assuming that these systems follow essentially first-order behavior between the asymptotic limits. It should be emphasized that the parameter space restrictions developed here are a result of assuming

that the derivation proceeds from an elementary reaction, reversible or irreversible, that is third-order. Kinetic data empirically modelled with a third-order polynomial in concentration need not remain within the presented parameter ranges. The analytic solution for $c''(z)$ remains valid, but the definition for Φ_G is not necessarily appropriate. Many possibilities for future work remain for the Dirichlet problem. For example, the impact of reverse reaction order has not been investigated. The enhancement in η_{int} for reversible reactions seems to derive from the diffusivities of the products, but this is not yet well understood or quantified. Solutions for zeroth-order reverse reactions, derived from the rules in this chapter, are presently valid only if the product species driving such a reaction is not consumed. This may or may not be possible, and could be restated to apply to the forward reaction. There is considerable overlap between the regions on an (η_{int}, Φ_G) plot described by reversible second and third-order reactions and various other kinetics, such as positive fractional-order kinetics and certain common Langmuir-Hinshelwood kinetic expression. There may be a theoretical link between some fractional order kinetics and the Weierstrass Pe-function type solutions presented here. Empirical kinetic modelling of catalytic reactions in porous media that has used Langmuir-Hinshelwood kinetics might well have been adequately modelled by second-order or third-order reversible kinetic expressions, since both can cover a large part of the region between $n = 0$ and $n = 1$ power law kinetics on an internal effectiveness factor versus generalized Thiele modulus plot.

CHAPTER 4
EXTENSIONS TO OTHER REACTION AND DIFFUSION PROBLEMS

Introduction

The previous two chapters have developed and explored the analytical solution for

the concentration profiles of conventional second-order and third-order reactions with

simultaneous diffusion in a slab-like medium for the Dirichlet boundary condition. From

here the development can proceed by branching in a number of different directions. The

procedures already developed can be extended to study the effect of using the Robin's

boundary condition, can be applied to the study of unconventional second-order and

third-order reactions, such as autocatalytic reactions, and can be broadened to include a

study of multiple reaction systems, e.g. parallel reactions, series-parallel reactions, and

so on. These subjects are the principal topics of this chapter.

Here it will be seen that, while the solution of the corresponding second-order and

third-order Robin's problems are possible, the present analysis is less ideal than could

be hoped. The elegance of the parameter space reductions used for the Dirichlet problem

is largely lost. The Robin's problem in its present state of development is one which

requires simultaneous solution of a pair of equations for specified free stream conditions.

These equations are generally both nonlinear. There is one format for the Robin's

problem that permits general study of its solution and which requires solution of only a

single nonlinear equation. Ideally this would also be the case for a practical problem where free stream concentrations and physical properties were specified. Future analysis may yield such a result.

This chapter will also explore why autocatalytic reactions cannot be considered conventional in the context of simultaneous reaction and diffusion in a slab. The problem will be developed for the Dirichlet boundary condition for second-order and third-order kinetics. The key feature of these reactions is that one (or more) species in the reaction appears on both the product side and the reactant side of the elementary reaction. The stoichiometric coefficient of such a species can, under certain conditions, take on a sign different from that of other species appearing in one of either the forward or reverse rate expression. When this occurs, it is possible for the square of the first-order modulus, Φ_{1st}^2, as defined in Chapters Two and Three to become negative. The internal effectiveness factor in this previously unexplored region can become much greater than unity, e.g. one million. It is also possible for the third-order modulus, X, to become negative when the autocatalysis involves third-order elementary reactions.

Finally, we will look at some applications of the Weierstrass elliptic Pe-function method to reaction systems characterized by more than a single extent of reaction. Specifically, the method can be applied to parallel reactions with power law kinetics to derive the concentration profile for a species undergoing competing forward reactions of third-order and/or second-order, combined with first-order or zeroth-order reactions. The analysis can also be applied to the initial portions of Van der Vusse kinetics. The discussion will also examine expressions for selectivity. Three different types of

selectivity will be examined. Selectivity depends on ratios of surface fluxes, which could be written as ratios of internal effectiveness factors for the various competing reactions. Conventionally, however, the internal effectiveness factor concept is only used minimally in these analyses.

The Robin's Problem

The Robin's problem, i.e. a significant external mass transfer resistance, is of nearly equal significance to the Dirichlet problem. The implicit Dirichlet boundary condition assumption, that external mass transfer can be neglected, is most often valid for gas or vapor phase systems, while the Robin's boundary condition is usually required for liquid phase systems. Numerous exceptions exist. The Robin's problem for simultaneous reaction and diffusion has not been studied in nearly the same detail as the Dirichlet problem in spite of its nearly equal importance. This is probably due in part to the complicating effect of the additional parameters introduced into the analysis through the boundary condition itself. Surface concentrations are no longer known, but they are related to known free stream concentrations. There is now a mass transfer coefficient for each species in addition to the set of properties required for the Dirichlet problem. Since reactions discussed in Chapter Three include up to six species, the analysis of the Robin's boundary condition for third-order kinetics will have to try and incorporate up to twelve new physical quantities (six mass transfer coefficients and six free stream concentrations). Up to six surface concentrations, contained in the Robin's boundary condition, will become values of the solution rather than part of the physical

data of the problem. Furthermore, the most fruitful dimensionless concentrations developed in Chapters Two and Three took differences between actual and surface concentrations. This approach will need to be modified in some manner to deal with unknown surface concentrations.

One possible solution procedure for the Robin's problem would be to convert it into one of the Dirichlet problems that have already been solved in Chapters Two and Three. Is this a real possibility? The boundary condition at the slab surface has been changed from

$$\hat{c}_i = \hat{c}_{is} \quad at \quad x = L \qquad\qquad 4.1$$

to

$$k_{gi}(\hat{c}_{if} - \hat{c}_{is}) = D_i\left(\frac{d\hat{c}_i}{dx}\right)_L \quad at \quad x = L. \qquad\qquad 4.2$$

Nevertheless, the interrelationship between species' concentrations in the slab

$$\frac{D_i}{v_i}(\hat{c}_i - \hat{c}_{is}) = \frac{D_j}{v_j}(\hat{c}_j - \hat{c}_{js}) \qquad\qquad 4.3$$

is still valid. The only problem seems to be that both $\hat{c}_{is}$ and $\hat{c}_{js}$ are unknown values of the concentration profile solution. At first glance it would seem that substituting eq. (4.3) into the original reaction rate expression, r_P, to eliminate $\hat{c}_j$ merely exchanges ignorance of $\hat{c}_j$ for ignorance of $\hat{c}_{is}$ and $\hat{c}_{js}$. Nonetheless, proceeding from this point one can then define a dimensionless concentration

$$c''(z) = \frac{D_i(\hat{c}_{is} - \hat{c}_i(x))}{v_i L^2 r_{P_s}} \qquad 4.4$$

as was done in Chapters Two and Three, where r_{P_s} also depends on all of the unknown surface concentrations $\hat{c}_{is}$, $\hat{c}_{js}$, etc. This approach leads to the same governing equations as those solved in Chapters Two and Three for the second-order and third-order Dirichlet problems. The boundary conditions are also the same as those for the Dirichlet problem thanks to the normalizations in eq. (4.4). The complicating factor is that the moduli, X, Ψ and Φ^2_{1st}, are implicit in the surface concentrations, so the concentration profile solution must be iterated until eq. (4.2) is satisfied for all species appearing in r_P.

One point in favor of this approach is that Chapters Two and Three have explored the behavior of the $c''(z)$ solution as a function of the three moduli in considerable detail. It is well behaved so that constructing a numerical scheme to iterate the moduli values to convergence via the Robin's boundary condition for each species is not expected to be too difficult. Also it will be seen below that the surface concentrations cannot be chosen independently of one another.

There is one further problem with this sort of approach that was first mentioned in Chapter One, namely that the dimensionless concentration created by eq. (4.4) leads to a dimensionless diffusion and reaction rate expression, r''_P, which is not generally valid in the free stream region. This occurred because eq. (4.3) was used to eliminate the other species in r_P and its range of validity did not extend to the free stream. So defining the overall effectiveness factor requires an alternative expression for the ratio

of the relative rates of reaction at the surface and in the free stream. Nevertheless, this approach to handling the Robin's boundary condition establishes that the slab interior problem retains the features discussed in Chapters Two and Three. The feasible ranges of the three moduli were not modified in any way by using the Robin's boundary condition.

Another possible approach is to write the surface derivatives of the species in terms of the internal effectiveness factor and surface reaction rate. This gives as many equations as there are species interrelating the surface concentrations and the internal effectiveness factor. This set can in principle be solved to eliminate all surface concentrations as functions of the internal effectiveness factor. The internal effectiveness factor squared already appeared in the two invariants of Chapter Three. No substitution was made there, but now it would make sense to do so. Then the equations for the dimensionless midplane concentration, $c''(0)$, and the internal effectiveness factor, η_{int}, would be solved simultaneously to complete the solution and find the moduli. Chapters Two and Three suggest that $2c''(0)$ is roughly about the same value as η_{int} for diffusion free and transitional behavior, and that they are both well behaved monotonic functions of the three moduli.

The relationship between the surface concentrations of different species must be examined in more detail. In the derivation of eq. (4.3) that appeared in Chapter One, there was a useful intermediate result, eq. (1.7), which is also still valid here

$$\frac{D_i}{v_i}\frac{d\hat{c}_i}{dx} = \frac{D_j}{v_j}\frac{d\hat{c}_j}{dx}.$$

4.5

Eqs. (4.2) and (4.5) can be combined to give

$$\frac{k_{gi}}{v_i}(\hat{c}_{if} - \hat{c}_{is}) = \frac{k_{gj}}{v_j}(\hat{c}_{jf} - \hat{c}_{js})$$

4.6

which relates $\hat{c}_{is}$ to $\hat{c}_{js}$ through the known free stream concentrations. This leads to the following relationship between $\hat{c}_i$ and $\hat{c}_j$

$$\hat{c}_j = \hat{c}_{jf} - \left(\frac{v_j}{v_i}\right)\left[\frac{k_{gi}}{k_{gj}}(\hat{c}_{if} - \hat{c}_{is}) + \frac{D_i}{D_j}(\hat{c}_{is} - \hat{c}_i)\right]$$

4.7

which can be used to eliminate all but one of the unknown surface concentrations in r_p in favor of the known free stream concentrations. The single species reaction and diffusion equation formed in this manner is still not generally valid in the free stream as can be seen by substituting $\hat{c}_i = \hat{c}_{if}$ into eq. (4.7). The free stream concentration of species J is not recovered unless the ratio of the species' diffusivities equals the ratio of the species' mass transfer coefficients. This is equivalent to having the Biot numbers for species I and J be equal. Algebraically, trying to create a single species diffusion and reaction rate expression which holds in the free stream and in the slab is like trying to have a line with two slopes. In other words there is little likelihood of ever obtaining linear relationships between different species that are valid both within the slab media and in the free stream. Using dimensional concentrations or simple ratios with the free stream concentrations appears to be the only way to deal with the problem at the present time. Nevertheless, eq. (4.7) substituted into r_p leads to a single species problem with

only a single unknown surface concentration, $\hat{c}_{is}$. Using the dimensionless concentration of eq. (4.4) leads as in Chapter Three to the following Dirichlet problem

$$\frac{d^2c''}{dz^2} = X c''^3 - \Psi c''^2 + \Phi^2_{1st}c'' - 1 \equiv r''_P \qquad 4.8$$

with boundary conditions

$$\frac{dc''}{dz} = 0 \quad at \quad z = 0, \quad c''(1) = 0 \quad at \quad z = 1. \qquad 4.9$$

The three moduli are given by eqs. (3.11-13) where eq. (4.6) is used to eliminate all but one surface concentration, $\hat{c}_{is}$, from r''_P, and the solution is subject to the constraint

$$Bi_{mi}c''_{if} = \left(\frac{dc''}{dz}\right)_{z=1} \qquad 4.10$$

where Bi_{mi} is the Biot number for mass transfer for species I, $k_{gi}L/D_i$, and c''_{if} is given by

$$c''_{if} = \frac{D_i(\hat{c}_{is} - \hat{c}_{if})}{v_i L^2 r_{Ps}(\hat{c}_{is})}. \qquad 4.11$$

Completing an analytical solution for a specific set of free stream concentrations, mass transfer coefficients, diffusivities, rate constants and characteristic length from this point requires simultaneous solution of the two equations below for $c''(0)$ and $\hat{c}_{is}$ or, less readily, c''_{if}:

$$c''(0) = -\frac{6[X(\hat{c}_{is})c''(0)^3 - \Psi(\hat{c}_{is})c''(0)^2 + \Phi_{1st}^2(\hat{c}_{is})c''(0) - 1]}{12\wp(1; g_2, g_3) - [3X(\hat{c}_{is})c''(0)^2 - 2\Psi(\hat{c}_{is})c''(0) + \Phi_{1st}^2(\hat{c}_{is})]} \quad 4.12$$

and

$$\frac{k_{gi}(\hat{c}_{is} - \hat{c}_{if})}{v_i L r_P(\hat{c}_{is})} = Bi_{mi}c''_{if} =$$

$$-\sqrt{-\frac{X(\hat{c}_{is})}{2}c''(0)^4 + \frac{2\Psi(\hat{c}_{is})}{3}c''(0)^3 - \Phi_{1st}^2(\hat{c}_{is})c''(0)^2 + 2c''(0)} \quad 4.13$$

where the dependence on $\hat{c}_{is}$ is indicated throughout. The two equations are preferably solved for $\hat{c}_{is}$ since this gives the three moduli more readily than c''_{if}. Note, however, that if one wants to study the Robin's problem in general, then the situation becomes noticeably simpler. It is then possible to start from any feasible surface concentration for one species and work the interior and exterior problems in series with no more complexity than was involved in solving the single nonlinear equation associated with the Dirichlet problem. This is the best approach developed to date and would certainly be useful to theoreticians.

The above formulations possess an interesting feature that becomes apparent even without completing the solution of the problem. The equations above and for the three moduli depend much more naturally on ratios of diffusivities and/or ratios of mass transfer coefficients than on ratios of a diffusivity with a mass transfer coefficient (Biot number). In the last of the above formulations the Biot number appears only for species

I, and never appears for the other species. This is an area for further study, namely what are the significant dimensionless external parameters for multiple species reaction and diffusion problems. This study suggests that the key parameters are really the k_{gi}/k_{gj} ratios possibly including a <u>single</u> Biot number for bridging between the external and internal transfer processes. In any event it is much harder to say that the analysis of the Robin's problem has reached as satisfactory a point as the analysis of the Dirichlet problem. There may be a clever way to formulate the problem so that the two nonlinear equations required for the finishing a solution can always be solved sequentially rather than simultaneously, for example, and not just for the case of assumed surface conditions. The main point to be made is that the Weierstrass elliptic Pe-function methodology developed in Chapters Two and Three is sufficient to formulate and solve the concentration profile problem for second-order and third-order reaction and diffusion in a slab with the Robin's boundary condition.

The Single Species Robin's Problem

The single species Robin's problem has been studied in detail for the irreversible first-order reaction; see Aris (1975). A plot can be prepared showing the effect of the Biot number on the overall effectiveness factor. Such a plot is made versus the Thiele modulus for first-order irreversible reactions which is also the generalized Thiele modulus. Such a plot is reproduced here in Figure 4.1. A Biot number of infinity corresponds to no mass transfer resistance between the free stream and the slab surface.

The analytical derivation in Aris leads to a sum of resistances formula for the overall effectiveness factor

$$\frac{1}{\eta_{overall}} = \frac{1}{\eta_{int}} + \frac{\Phi_G^2}{Bi_m} \qquad 4.14$$

where $\Phi_G^2 = k_f L^2 / D_A$ and A is taken as the reacting species. For second-order and third-order reactions there is a choice to be made as to which concentration, surface or free stream, will be used in defining the problem moduli. To compare between different reaction orders, I have chosen to use the surface concentration in defining the higher order reaction moduli. This permits asymptotic matching of the internal effectiveness factor for first-order, second-order and third-order irreversible single species reactions, when plotted against the generalized Thiele modulus. Consequently, differences in behavior due to reaction order and Biot number must manifest themselves in the overall effectiveness factor primarily through the external effectiveness factor. For the third-order Robin's problem, $3A \rightarrow$ products, the generalized Thiele modulus is given by

$$\Phi_G^2 = \frac{6L^2 k_f \hat{c}_{As}^2}{D_A} = 6\Phi_{AAA}^2 \qquad 4.15$$

while for the second-order case, $2A \rightarrow$ products, the generalized Thiele modulus is given by

$$\Phi_G^2 = \frac{3L^2 k_f \hat{c}_{As}}{D_A} = 3\Phi_{2A}^2 . \qquad 4.16$$
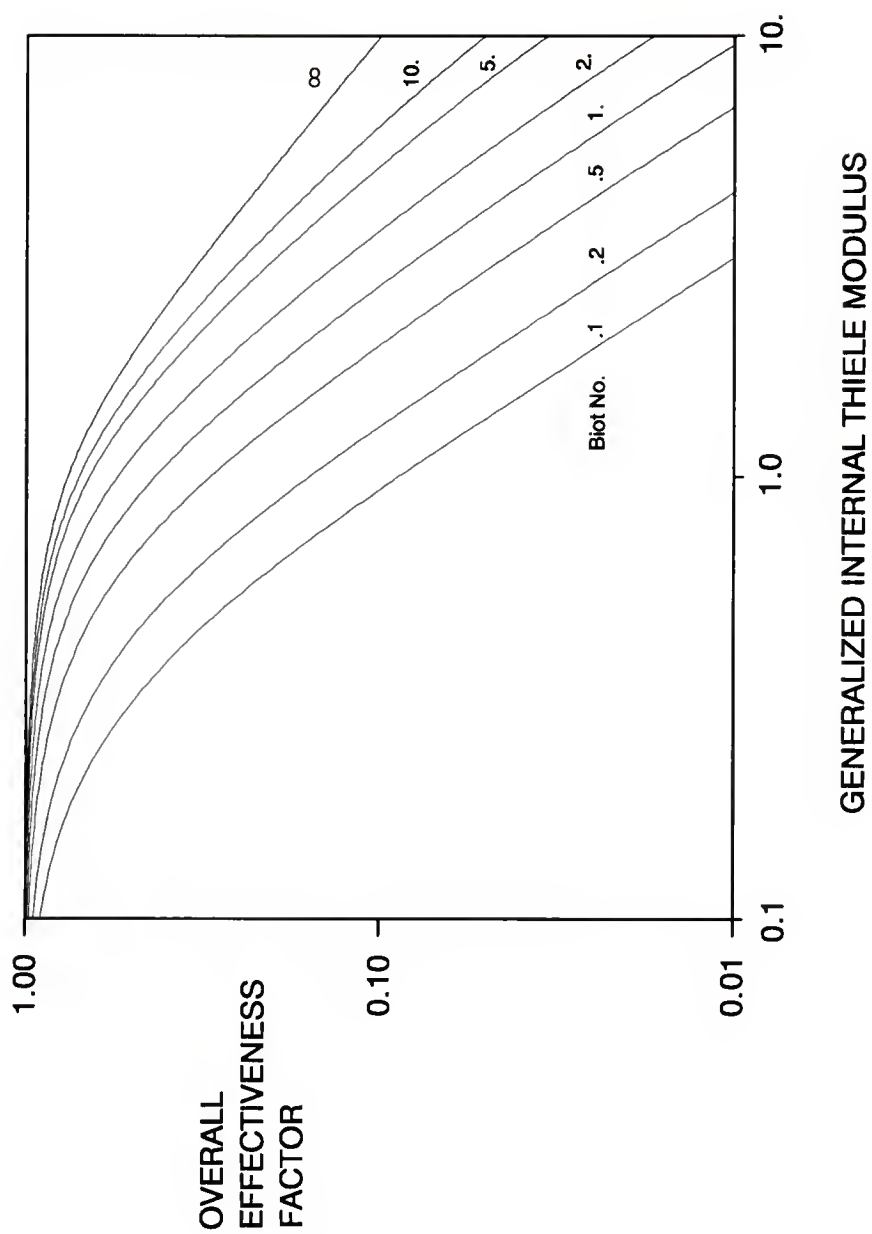
Figure 4.1 Overall effectiveness factor for first-order reactions as a function of Biot number and generalized Thiele modulus.

No linear substitutions for secondary species are required in the single species case. Consequently the dimensionless reaction and diffusion rate expression in this special case is valid both in the free stream and within the slab. The Robin's boundary condition can be written in terms of the internal effectiveness factor as

$$Bi_m c''_f = \left(\frac{dc''}{dz}\right)_{z=1} = -\eta_{int} . \qquad \qquad 4.17$$

The overall effectiveness factor can be expanded as the product of the internal effectiveness factor and the external effectiveness factor to give

$$\eta_{overall} = \frac{-1}{r''_P(c''_f)} \cdot \eta_{int} \qquad \qquad 4.18$$

since $r''_P = -1$ at the slab surface. The three moduli for the irreversible single species third-order reaction can all be written in terms of a single species modulus as shown in eq. (3.36). When this information is substituted into the dimensionless reaction rate expression, eq. (4.18) simplifies to

$$\eta_{overall} = \frac{-\eta_{int}}{27\,\Phi_{AAA}^6 c''^3_f - 27\,\Phi_{AAA}^4 c''^2_f + 9\,\Phi_{AAA}^2 c''_f - 1} . \qquad \qquad 4.19$$

Eq. (4.17) can be used to eliminate the dimensionless free stream concentration from eq. (4.19). Eq. (4.15) can be used to switch from Φ_{AAA}^2 to Φ_G^2 in eq. (4.19). The results can be put into a sum of resistances format to give

$$\frac{1}{\eta_{overall}} = \frac{1}{\eta_{int}} + \frac{3\,\Phi_G^2}{2Bi_m} + \frac{3\,\Phi_G^4\eta_{int}}{4Bi_m^2} + \frac{\Phi_G^6\eta_{int}^2}{8Bi_m^3} \qquad 4.20$$

as the third-order analog to eq. (4.14). Remember that there is a known one-to one relationship between Φ_G and η_{int}. Thus $\eta_{overall}$ can be said to depend on either one of these plus the Biot number. In this form it is obvious that the overall effectiveness factor for the irreversible single species third-order reaction will always be less than that for the irreversible first-order reaction with equivalent values of the generalized Thiele modulus and Biot number. Proceeding similarly with eqs. (4.16) and (2.97) for the irreversible single species second-order reaction leads to

$$\frac{1}{\eta_{overall}} = \frac{1}{\eta_{int}} + \frac{4\,\Phi_G^2}{3Bi_m} + \frac{4\,\Phi_G^4\eta_{int}}{9Bi_m^2} \qquad 4.21$$

where $\eta_{overall}$ also obviously takes on smaller values than in eq. (4.14) for equivalent Biot numbers and Φ_G. It should also be apparent that the overall effectiveness factor for the single species irreversible second-order reaction will be larger than that for the comparable third-order reaction given by eq. (4.20) for the same values of the generalized Thiele modulus and Biot number. That this is the case is illustrated in Figure 4.2 where overall effectiveness factors for both second-order and third-order single species reactions are plotted versus the generalized Thiele modulus for the same values of the Biot number that were used in Figure 4.1.
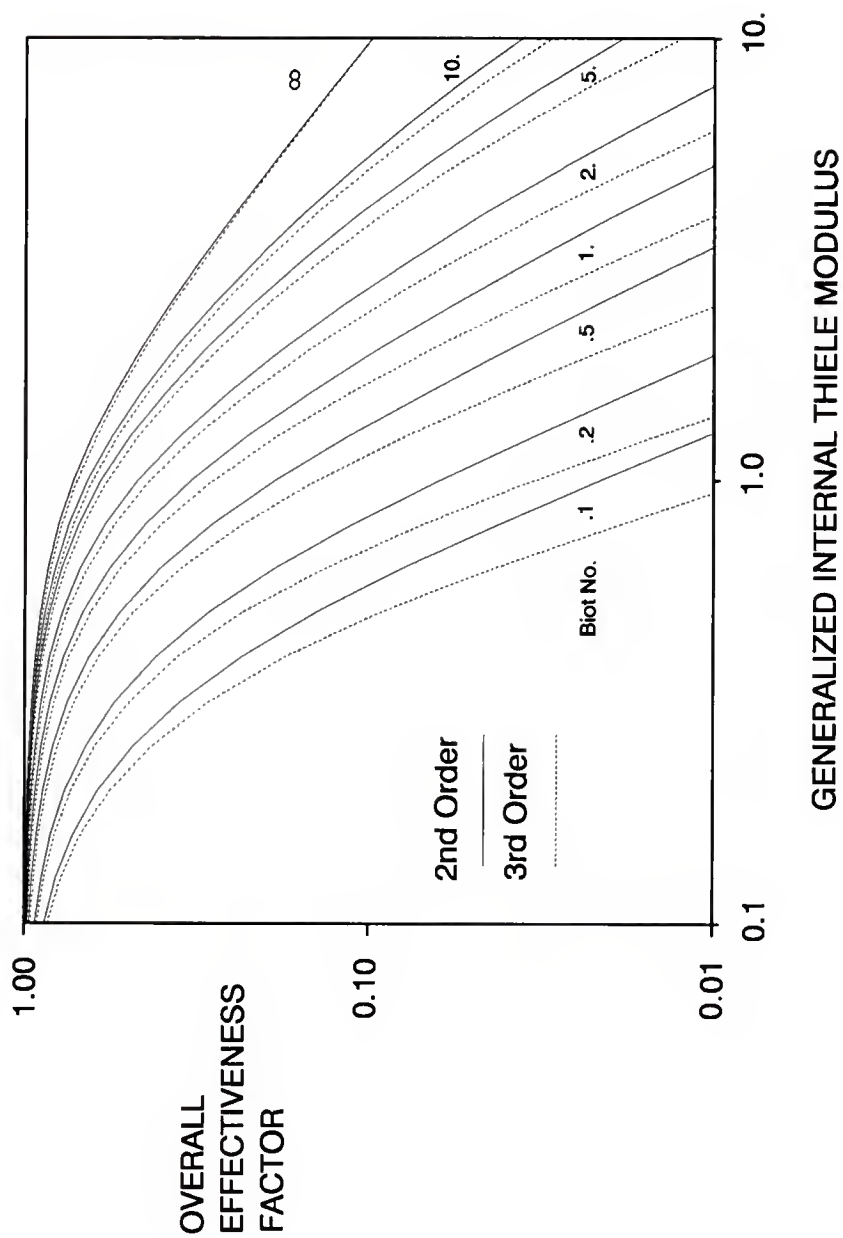
Figure 4.2 Overall effectiveness factor for single species irreversible second-order and third-order reactions as a function of the Biot number and generalized Thiele modulus.

To this point the analysis indicates that, under conditions when the efficiency of the internal reaction and diffusion problem are comparable for all rate expressions, the overall effectiveness factor decreases with increasing reaction order at constant Biot number. This is an important result, but there is a practical difficulty. Except for first-order reactions, the generalized Thiele modulus is not *a priori* known, since the surface concentration is part of the solution of the problem, not part of the original data. The definition of the internal effectiveness factor for the slab with power law kinetics of the type used here containing stoichiometric coefficients is given by

$$\eta_{int} = \frac{D_A \left(\dfrac{d\hat{c}_A}{dx}\right)_L}{L n k_f \hat{c}_{As}^n} \, . \qquad 4.22$$

Combining eq. (4.22) with the Robin's boundary condition, eq. (4.2) gives

$$\left(\frac{k_{gA}L}{D_A}\right)\left(\frac{\hat{c}_{Af}}{\hat{c}_{As}} - 1\right) = \left(\frac{L^2 n k_f \hat{c}_{As}^{n-1}}{D_A}\right)\eta_{int} = \frac{2}{n+1}\Phi_G^2 \eta_{int} \qquad 4.23$$

after some rearrangement. A so-called "observable Thiele modulus" can be defined by analogy with the generalized Thiele modulus by substituting the free stream concentration for the surface concentration

$$\Phi_F^2 \equiv \left(\frac{n+1}{2}\right)\left(\frac{L^2 n k_f \hat{c}_{Af}^{n-1}}{D_A}\right) . \qquad 4.24$$

This free stream based Thiele modulus does not possess much particular physical significance, since it combines a free stream quantity with internal properties of the slab reaction and diffusion problem. Eq. (4.23) and eq. (4.24) can be combined with the definition of the Biot number to yield

$$\Phi_F^2 = \Phi_G^2 \left[\frac{(n+1)Bi + 2\Phi_G^2\eta_{int}}{(n+1)Bi} \right]^{n-1} \qquad 4.25$$

which relates the observable Thiele modulus to the Biot number and generalized Thiele modulus. Figure 4.3 plots this relationship for both second-order and third-order power law kinetics at the same values of the Biot number used throughout. Figures 4.2 and 4.3 taken together give a complete solution of the Robin's problem's overall effectiveness factor for specified free stream concentration and Biot number. Eqs. (4.20-21) could be redeveloped in terms of Φ_F^2 and Figure 4.2 could be replotted versus Φ_F instead of Φ_G. Such topics are not explored further here, but one should note the following points. First, the zeroth-order reaction develops a family of curves at fixed Biot numbers on a plot of $\eta_{overall}$ versus Φ_F. There was no such family of curves when plotted against Φ_G, since the external effectiveness factor is unity for all Biot numbers. Second, the trend of the overall effectiveness factor from zeroth-order through third-order is that it increases with increasing reaction order at constant Φ_F and Biot number. In other words the trend is reversed from that obtained when plotting versus Φ_G.

This look at the single species cases of higher order reaction and diffusion with the Robin's boundary condition gives the first ever look at the relative importance of the
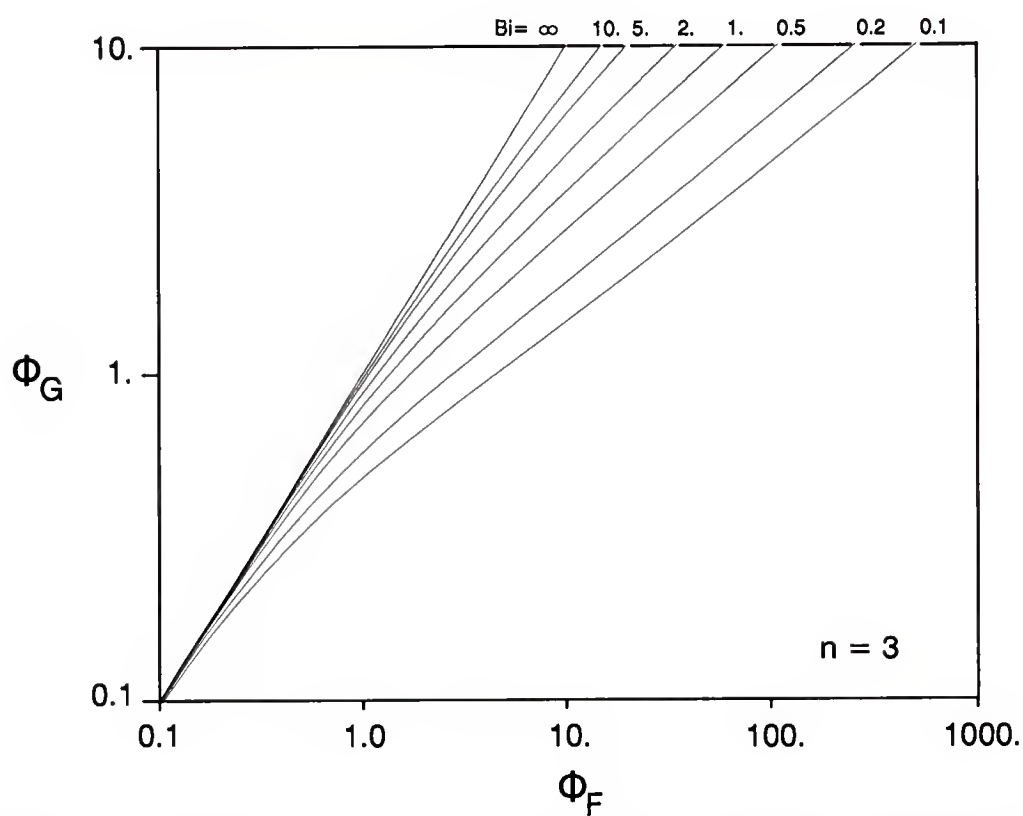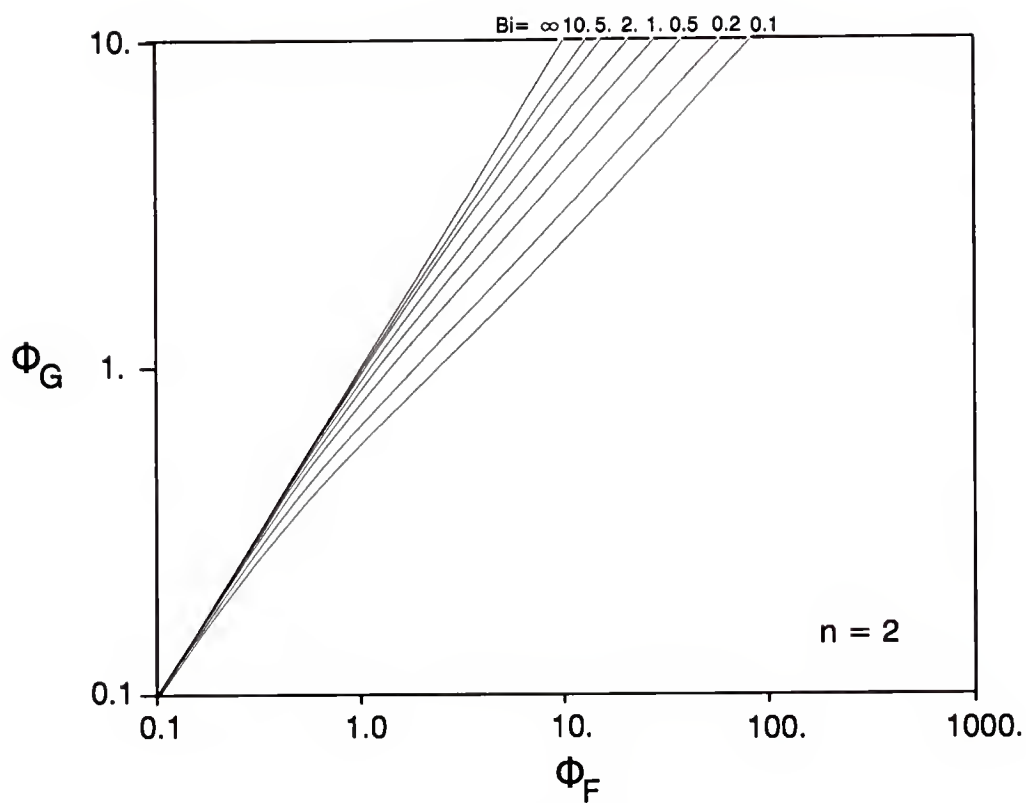
Figure 4.3 Relationship between the observable Thiele modulus and the generalized Thiele modulus for second-order and third-order power law kinetics.

external transfer resistance for various power law reaction orders. The trends indicate that the deleterious effects of a significant external mass transfer resistance are magnified by higher reaction orders. Whether this will be true in general for multiple species second-order and third-order reaction and diffusion systems is an area for further study.

Autocatalytic Reactions

Another fruitful area of research in higher order reactions is the examination of autocatalytic kinetics occurring in media. This is particularly true since it is difficult to construct a first-order analog to an autocatalytic reaction. While there are many formal definitions of autocatalysis, for our purposes autocatalysis will be defined as a reaction where a "reactant" species has a positive, rather than a negative, stoichiometric coefficient. Examples of such elementary reactions that are also net second-order or third-order are given in Table 4.1. The reactions listed in Table 4.1 are not intended to be all inclusive unlike the attempts made in Table 2.1 and Table 3.1 for conventional elementary second-order and third-order reactions respectively. For these autocatalytic reactions one generally gets v_A equal to one, or possibly two, instead of minus one or minus two. It is possible to write elementary reactions, such as $A \rightarrow 2A + P$, which qualify on stoichiometric coefficient grounds as an autocatalytic reaction but obviously violate conservation of mass principles. It is also possible to set up competing autocatalysis with a reaction such as $2A + B \rightleftarrows 2B + A$, where B catalyses the forward reaction and A catalyses the reverse reaction. So there are some pretty interesting kinetic schemes to consider in the context of net second-order and third-order reaction and

Table 4.1 Typical Elementary Autocatalytic Reactions

Case	Stoichiometry	Rate Expression
1	$A + B \rightleftarrows 2A$	$r_P = k_r \hat{c}_A^2 - k_f \hat{c}_A \hat{c}_B$
2	$A + B \rightarrow 2A$	$r_P = -k_f \hat{c}_A \hat{c}_B$
3	$A + B + C \rightleftarrows 2A + P$	$r_P = k_r \hat{c}_A^2 \hat{c}_P - k_f \hat{c}_A \hat{c}_B \hat{c}_C$
4	$A + 2B \rightleftarrows 2A + P$	$r_P = k_r \hat{c}_A^2 \hat{c}_P - k_f \hat{c}_B^2 \hat{c}_A$
5	$A + B + C \rightleftarrows 3A$	$r_P = k_r \hat{c}_A^3 - k_f \hat{c}_A \hat{c}_B \hat{c}_C$
6	$2A + B \rightleftarrows 3A$	$r_P = k_r \hat{c}_A^3 - k_f \hat{c}_A^2 \hat{c}_B$
7	$A + B + C \rightleftarrows 2A$	$r_P = k_r \hat{c}_A^2 - k_f \hat{c}_A \hat{c}_B \hat{c}_C$
8	$A + B \rightleftarrows 2A + P$	$r_P = k_r \hat{c}_A^2 \hat{c}_P - k_f \hat{c}_A \hat{c}_B$
9	$A + B \rightleftarrows 3A$	$r_P = k_r \hat{c}_A^3 - k_f \hat{c}_A \hat{c}_B$
10	$A + B + C \rightarrow 2A + P$	$r_P = -k_f \hat{c}_A \hat{c}_B \hat{c}_C$
11	$A + 2B \rightarrow 2A + P$	$r_P = -k_f \hat{c}_B^2 \hat{c}_A$
12	$A + B + C \rightarrow 3A$	$r_P = -k_f \hat{c}_A \hat{c}_B \hat{c}_C$
13	$2A + B \rightarrow 3A$	$r_P = -k_f \hat{c}_A^2 \hat{c}_B$
14	$A + B + C \rightarrow 2A$	$r_P = -k_f \hat{c}_A \hat{c}_B \hat{c}_C$
15	$A + B \rightarrow 2A + P$	$r_P = -k_f \hat{c}_A \hat{c}_B$
16	$A + B \rightarrow 3A$	$r_P = -k_f \hat{c}_A \hat{c}_B$
17	$2A + B \rightleftarrows A + 2B$	$r_P = k_r \hat{c}_B^2 \hat{c}_A - k_f \hat{c}_A^2 \hat{c}_B$

diffusion in a slab. The solution of second-order and third-order problems of autocatalysis is the subject of this section.

The analysis of the Dirichlet problem proceeds exactly as in Chapter Three in terms of the preferred dimensionless concentration, c''(z). The same three moduli appear as in eqs. (3.11-3.13)

$$\Phi_{1st}^2 = L^2 \left(\frac{\nu_Q k_r \hat{c}_{Ps} \hat{c}_{Rs}}{D_Q} + \frac{\nu_P k_r \hat{c}_{Rs} \hat{c}_{Qs}}{D_P} + \frac{\nu_R k_r \hat{c}_{Qs} \hat{c}_{Ps}}{D_R} - \right.$$
$$\left. \frac{\nu_C k_f \hat{c}_{As} \hat{c}_{Bs}}{D_C} - \frac{\nu_A k_f \hat{c}_{Bs} \hat{c}_{Cs}}{D_A} - \frac{\nu_B k_f \hat{c}_{Cs} \hat{c}_{As}}{D_B} \right) \qquad 4.26$$

$$\Psi = L^4 \left(\frac{\nu_R \nu_Q k_r \hat{c}_{Ps}}{D_R D_Q} + \frac{\nu_P \nu_Q k_r \hat{c}_{Rs}}{D_P D_Q} + \frac{\nu_P \nu_R k_r \hat{c}_{Qs}}{D_P D_R} - \frac{\nu_B \nu_C k_f \hat{c}_{As}}{D_B D_C} - \right.$$
$$\left. \frac{\nu_A \nu_C k_f \hat{c}_{Bs}}{D_A D_C} - \frac{\nu_A \nu_B k_f \hat{c}_{Cs}}{D_A D_B} \right) (k_r \hat{c}_{Ps} \hat{c}_{Rs} \hat{c}_{Qs} - k_f \hat{c}_{As} \hat{c}_{Bs} \hat{c}_{Cs}) \qquad 4.27$$

$$X = L^6 \left(\frac{\nu_P \nu_R \nu_Q k_r}{D_P D_R D_Q} - \frac{\nu_A \nu_B \nu_C k_f}{D_A D_B D_C} \right) (k_r \hat{c}_{Ps} \hat{c}_{Rs} \hat{c}_{Qs} - k_f \hat{c}_{As} \hat{c}_{Bs} \hat{c}_{Cs})^2. \qquad 4.28$$

The rules for adapting these equations to specific elementary reactions, as given in Chapter Three, did not allow for the possibility that a single species might be both a reactant and a product. The rules apply nonetheless. Species that are both product and reactant have one and only one value for their stoichiometric coefficient. They do not have a product side stoichiometric coefficient and a reactant side stoichiometric

coefficient. So if R and Q are in reality species A, while B, C and P are not, than v_A is $+1$ as are v_R and v_Q. That is the extent of any additional interpretation required to write down the moduli expansions for autocatalytic reactions.

The implications of reversing the sign of a stoichiometric coefficient on the first-order and third-order moduli are obvious from eqs. (4.26) and (4.28). No longer must Φ^2_{1st} or X be positive valued only as was the case for conventional reactions. New regions of feasible parameter space become available for autocatalytic reactions that were denied to the elementary conventional second-order and third-order reactions discussed in Chapters Two and Three. The shape of the allowed moduli regions must be redeveloped for autocatalytic reactions. Then the analytical solution must be studied in regions outside those already discussed in the earlier chapters. Although work in this area is ongoing, a complete story can be told for the case of second-order autocatalytic reactions.

Consider the reaction $A + B \rightleftarrows 2A$ where A is the autocatalytic species. The first-order and second-order moduli can be developed from eqs. (4.26-4.27) to give

$$\Phi^2_{1st} = \left(\frac{k_r L^2 \hat{c}_{As}}{D_A} + \frac{k_f L^2 \hat{c}_{As}}{D_B} \right) + \left(\frac{k_r L^2 \hat{c}_{As}}{D_A} - \frac{k_f L^2 \hat{c}_{Bs}}{D_A} \right)$$

$$= (\Phi^2_{2A} + \Phi^2_{A+B}) + (\Phi^2_{2A} - \Phi^2_{B+A}) \qquad 4.29$$

$$\Psi = \left(\frac{k_r L^2 \hat{c}_{As}}{D_A} + \frac{k_f L^2 \hat{c}_{As}}{D_B} \right)\left(\frac{k_r L^2 \hat{c}_{As}}{D_A} - \frac{k_f L^2 \hat{c}_{Bs}}{D_A} \right)$$

$$= (\Phi^2_{2A} + \Phi^2_{A+B})(\Phi^2_{2A} - \Phi^2_{B+A}) \qquad 4.30$$

after simplifying and rearranging terms. Expressions like these reveal that when Ψ is positive, Φ^2_{1st} must also be positive. This is true in general for second-order autocatalytic reactions. When solving the problem: maximize Ψ subject to constant Φ^2_{1st} for nonnegative irreversible reaction species moduli, this restriction on Ψ is also developed. The constraint in Chapter Two, $\Psi \leq \Phi^4_{1st}/4$, could be derived without requiring that the inequality constraints for nonnegative irreversible reaction Thiele moduli be active for the strictly positive Φ^2_{1st} considered there. These constraints are active for negative Φ^2_{1st} and deny the region $0 \leq \Psi \leq \Phi^4_{1st}/4$ in those cases. The region of positive Ψ remains available for positive values of Φ^2_{1st} with autocatalytic reactions. The parameter space thus includes the entire space for conventional second-order reactions studied in Chapter Two plus the additional quadrant defined by $\Phi^2_{1st} < 0$, $\Psi < 0$.

The behavior of the solution discussed in Chapter Two must be extended to cover the additional parameter space territory just described. Figure 4.4 presents results for the region of negative Φ^2_{1st} for second-order autocatalytic reactions. A very pronounced autocatalytic boost in internal effectiveness factor is observed for small magnitudes of Ψ. Physically, this region is most easily reached by having a pronounced shortage of the autocatalytic species at the slab surface along with a favorable forward reaction rate constant. The reaction is very much diffusion controlled in the high internal effectiveness factor region. That happens to be good in this case, since the concentration variation of the autocatalytic species from surface to midplane is what is driving the increase in interior reaction rates relative to the surface. It is worth pointing out that c''(0) is no longer bound above by one-half. This bound presumes that the maximum
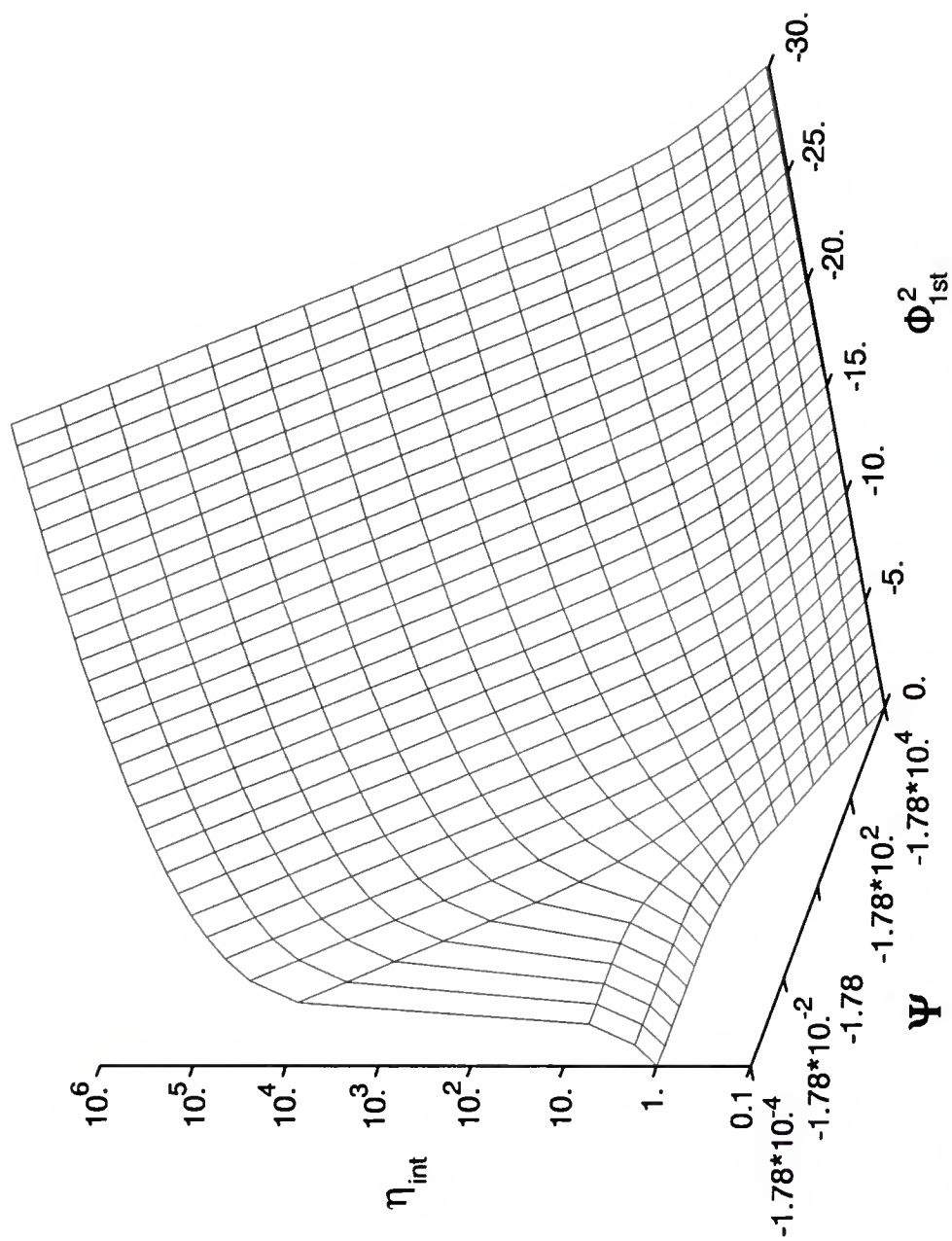
Figure 4.4 Internal effectiveness factor for second-order autocatalytic reactions in the newly opened region of parameter space.

reaction rate occurs at the slab surface. This is no longer necessarily the case for autocatalytic reactions.

Examination of the region of negative Φ_{1st}^2 and small Ψ suggested the following prototype first-order model

$$D\frac{d^2\hat{c}}{dx^2} = -k\hat{c} \qquad\qquad 4.31$$

where the negative sign on the rate constant is the only unusual feature. This equation linked with the Dirichlet boundary conditions has the solution

$$\frac{\hat{c}(x/L)}{\hat{c}_s} = \frac{\cos(\Phi x/L)}{\cos(\Phi)} \qquad \Phi = \sqrt{L^2 k/D} \qquad 4.32$$

and internal effectiveness factor

$$\eta_{int} = \frac{tan(\Phi)}{\Phi}. \qquad\qquad 4.33$$

Clearly this solution cannot be accepted generally, because the cosine function is not necessarily positive. However, the solution can be considered on the interval $0 < \Phi < \pi/2$. Over most of this range, eqs. (4.32) and (4.33) with $\Phi^2 = -\Phi_{1st}^2$ are in close agreement with the internal effectiveness factor results in Figure 4.4 at $\Psi = -1.78*10^{-4}$ and also with their corresponding midplane concentrations. As Ψ goes to zero, this agreement appears to become perfect over most ($\sim 95\%$) of the allowed interval. The
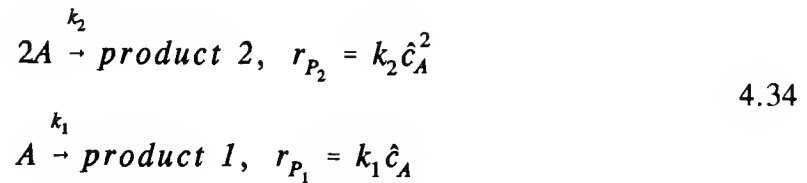
lowermost possible limit for Φ_{1st}^2 would be $-\pi^2/4$, or about -2.5. This then is a crude first-order prototype to autocatalytic behavior. It lacks the natural control features of the second-order reactions, e.g. consumable reactants or reversible reactions, but still captures the region of rapid increase in η_{int} shown in Figure 4.4. The second-order solution in terms of the Weierstrass Pe-function, however, is much better behaved than this crude first-order prototype as Ψ goes to zero for more negative values of Φ_{1st}^2. It does not develop oscillations in sign or periodicities over the ranges studied to date.

The detailed study of autocatalytic reactions needs to be extended to third-order reactions. The analytical solution is in hand. Since these reactions possess a first-order modulus, presumably it is safe to say that they will also possess parameter regions where the internal effectiveness factor exceeds unity. This may or may not also be triggered by negative values of X alone or in concert with some constraints on the other moduli. Many of the reactions in Table 4.1 could be studied in their own right rather than in a general third-order sense, and the results could be compared and contrasted. Such studies have only barely begun to examine and compare a few of the conventional second-order and third-order reactions.

Multiple Reaction Systems

The versatility of the Weierstrass elliptic Pe-function formulation begins to break down beyond systems characterized by a single extent of reaction, e.g. all those discussed to this point. The $\wp$ function solves a class of equivalent ordinary differential equations, see Ince (1927), and is not easily applied to problems with more than a single

ordinary differential equation. The powerful theories of linear mathematics which help to establish the extensions of solution methods for single linear ODE problems to systems of multiple coupled linear ODE's do not often find application in the nonlinear problems under discussion here. This leads to a trial and error search of potential second-order and third-order multiple reaction system candidates that can be reduced to a single ODE with a third-order or lower polynomial diffusion and reaction rate expression. The first such system found was

$$2A \xrightarrow{k_2} product\ 2, \quad r_{P_2} = k_2 \hat{c}_A^2$$
$$A \xrightarrow{k_1} product\ 1, \quad r_{P_1} = k_1 \hat{c}_A \tag{4.34}$$

with the single governing ODE

$$D_A \frac{d^2 \hat{c}_A}{dx^2} = 2k_2 \hat{c}_A^2 + k_1 \hat{c}_A. \tag{4.35}$$

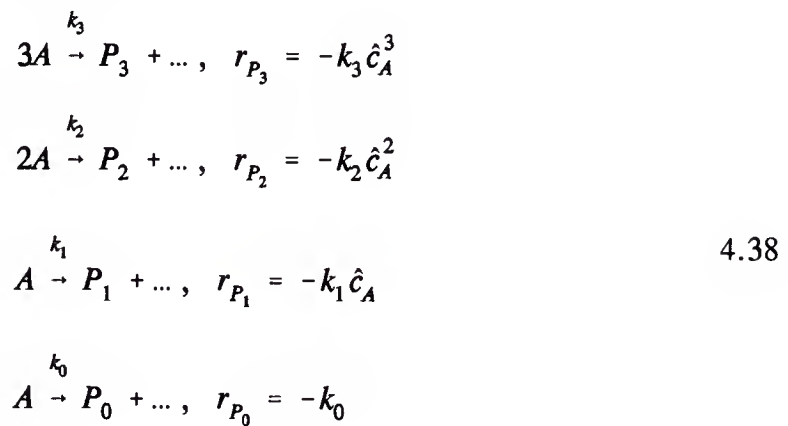This is a single ODE with a net second-order reaction rate expression without any further manipulations. The concentration profile and surface flux for species A can be derived easily from the methods described in the previous chapters. The solution is

$$c_A(z) = c_A(0) + \frac{\Phi_{2A}^2 c_A^2(0) + \Phi_A^2 c_A(0)/2}{\wp(z; g_2, g_3) - \Phi_{2A}^2 c_A(0)/3 - \Phi_A^2/12} \tag{4.36}$$

where $g_2 = \Phi_A^4/12$ and

$$g_3 = \frac{\Phi_{2A}^4(4\,\Phi_{2A}^2 c_A^3(0) - 3\,\Phi_A^2 c_A^2(0))}{27} - \frac{\Phi_A^6}{216}.$$ 4.37

The irreversible reaction Thiele moduli are defined per the definitions in Chapter Two. Having found this extension, it was obvious that the Weierstrass Pe-function methods would apply generally to any subset of

$$3A \xrightarrow{k_3} P_3 + \dots, \quad r_{P_3} = -k_3 \hat{c}_A^3$$

$$2A \xrightarrow{k_2} P_2 + \dots, \quad r_{P_2} = -k_2 \hat{c}_A^2$$

$$A \xrightarrow{k_1} P_1 + \dots, \quad r_{P_1} = -k_1 \hat{c}_A \qquad\qquad 4.38$$

$$A \xrightarrow{k_0} P_0 + \dots, \quad r_{P_0} = -k_0$$

with governing equation

$$D_A \frac{d^2 \hat{c}_A}{dx^2} = 3k_3 \hat{c}_A^3 + 2k_2 \hat{c}_A^2 + k_1 \hat{c}_A + k_0.$$ 4.39

Not all of the k_i, $i=0,1,2,3$, must be nonzero. The key result here is that parallel reactions of different order for a single species can be studied analytically using the Weierstrass elliptic Pe-function solution.

The underlying issue in studying reaction systems such as eq. (4.38) or other multiple reaction systems generally becomes one of selectivity. Selectivity is subject to a certain amount of interpretation so no one definition is universal. In simultaneous reaction and diffusion problems it is generally taken to be the ratio of two slab averaged

rates of reaction, one for a desired reaction and one for either an undesired reaction or an overall reactant consumption expression. Wheeler (1951) defined three types of selectivity for product distributions influenced by simultaneous diffusion and reaction. Type I selectivity is for simultaneous reactions, e.g.

$$A \rightarrow Products$$
$$B \rightarrow Products$$

4.40

as an example of the simplest case. Selectivity for this system could be defined as

$$S(A/B) = \frac{D_A (d\hat{c}_A/dx)_{x=L}}{D_B (d\hat{c}_B/dx)_{x=L}}$$

4.41

for the relative selectivity of A relative to B, or as

$$S(A) = \frac{D_A (d\hat{c}_A/dx)_{x=L}}{D_A (d\hat{c}_A/dx)_{x=L} + D_B (d\hat{c}_B/dx)_{x=L}}$$

4.42

for the relative selectivity of A relative to the total reaction rate of both A and B. Type II selectivity is for parallel reactions, e.g. systems such as eqs. (4.34) and (4.38). For the system in eq. (4.38) selectivity could be defined either as

$$S(P/R) = \frac{D_P (d\hat{c}_P/dx)_{x=L}}{D_R (d\hat{c}_R/dx)_{x=L}}$$

4.43

for selectivity defined as the ratio between two different product formation rates, illustrated here for P and R, or as

$$S(P/A) = \frac{D_P(d\hat{c}_P/dx)_{x=L}}{D_A(d\hat{c}_A/dx)_{x=L}} \qquad 4.44$$

for the selectivity of the formation of some product, e.g. P, relative to the total rate of consumption of the principal reactant A, i.e. what fraction of consumed A forms P.

Type III selectivity refers to consecutive or series type reactions, for example

$$A \rightarrow B \rightarrow C. \qquad 4.45$$
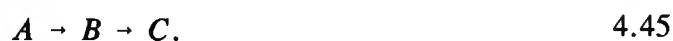
Selectivity here is usually taken to mean

$$S(B/C) = \frac{D_B(d\hat{c}_B/dx)_{x=L}}{D_C d\hat{c}_C/dx)_{x=L}} \qquad 4.46$$

the ratio of the formation rates of the intermediate and final product with no reference to A; see Roberts (1972). There are certain variations on these three themes such as the so called Van der Vusse problem as described in Carberry (1976), where the elementary reactions take the following form

$$A \overset{k_1}{\rightarrow} B \overset{k_2}{\rightarrow} C$$
$$2A \overset{k_3}{\rightarrow} D. \qquad 4.47$$

Van der Vusse himself (1966) has actually studied the reaction and diffusion problem in a slab for the system

$$A + B \xrightarrow{k_1} C$$

$$A + C \xrightarrow{k_2} D. \tag{4.48}$$

under the assumption that the concentration of reactant A is constant in the slab. Then eq. (4.48) can be simplified to Type III selectivity, $B \rightarrow C \rightarrow D$. Van der Vusse briefly describes some numerical results for cases where either the reaction $B \rightarrow C$ or the reaction $C \rightarrow D$ is second-order and the other reaction is first-order or zeroth-order. In other words, he really studied the problem

$$D_B \frac{d^2\hat{c}_B}{dx^2} = k_1 \hat{c}_B^m$$

$$D_C \frac{d^2\hat{c}_C}{dx^2} = k_2 \hat{c}_C^n - k_1 \hat{c}_B^m \tag{4.49}$$

for the cases of $(m,n) = (2,0)$, $(2,1)$, $(2,2)$, $(1,2)$, and $(0,2)$. He used an analog computer to model the ODE's. Clearly the first governing equation in eq. (4.49) is immediately solvable analytically when $m = 2$ using the Weierstrass elliptic Pe-function procedure described in Chapter Two. The second governing equation does not appear solvable for $n = 2$ for any of these m using the Weierstrass elliptic Pe-function procedures. Further analysis is possible for $n = 1$ or $n = 0$ when $m = 2$. One can find the homogeneous solution for $\hat{c}_C$ unforced by $k_1 \hat{c}_B^2(x)$, and apply conventional methods to obtain a particular solution of the inhomogeneous problem. This will contain integrals

of the forcing function, but this is generally a better situation than having an unsolved ODE. The procedure will be illustrated below for a very similar problem to eq. (4.49).

Carberry's Van der Vusse elementary reaction system, A → B → C and 2A → D, is an example of a system which yields partially to analysis with the Weierstrass elliptic Pe-function. The dimensionless governing equations for the four species are

$$\frac{d^2 c_A}{dz^2} = 2\Phi_{2A}^2 c_A^2 + \Phi_A^2 c_A \qquad 4.50$$

$$\frac{d^2 c_B}{dz^2} = -\Gamma_{AB}\Phi_A^2 c_A + \Phi_B^2 c_B \qquad 4.51$$

$$\frac{d^2 c_C}{dz^2} = -\Gamma_{BC}\Phi_B^2 c_B \qquad 4.52$$

$$\frac{d^2 c_D}{dz^2} = -\Gamma_{AD}\Phi_{2A}^2 c_A^2 \qquad 4.53$$

where the irreversible reaction Thiele moduli and the Γ_{ij} are defined using the notational conventions in Chapter Two. The equation for c_A is in the form solved throughout Chapter Two. For Dirichlet boundary conditions, the solution is

$$c_A(z) = c_A(0) + \frac{6\Phi_{2A}^2 c_A^2(0) + 3\Phi_A^2 c_A(0)}{6\wp(z; \Phi_A^4/12, g_3) - 2\Phi_{2A}^2 c_A(0) - \Phi_A^2/2} \qquad 4.54$$

which is just a modified version of eq. (4.36) above. The analysis for c_B is made using the method of variation of parameters given in many standard mathematical texts

including Gillett (1970). Assume that two functions, v_1 and v_2, exist such that $c_{BP} = v_1 sinh(\Phi_B z) + v_2 cosh(\Phi_B z)$ is a particular solution of the governing equation for c_B, which has the familiar homogeneous solution $c_{BH} = a_1 sinh(\Phi_B z) + a_2 cosh(\Phi_B z)$, where a_1 and a_2 are constants equal to zero and $1/cosh(\Phi_B)$ respectively here. If one requires that, in addition to satisfying the governing equation,

$$v'_1 sinh(\Phi_B z) + v'_2 cosh(\Phi_B z) = 0 \qquad 4.55$$

then

$$\Phi_B v'_1 cosh(\Phi_B z) + \Phi_B v'_2 sinh(\Phi_B z) = -\Phi_A^2 \Gamma_{AB} c_A(z). \qquad 4.56$$

where the prime denotes differentiation with respect to z for the only time in this work. This leads to the following expression for the particular solution of c_B

$$c_{BP}(z) = \frac{\Phi_A^2 \Gamma_{AB}}{\Phi_B^2}\left[sinh(\Phi_B z)\int_z^1 c_A(\alpha)cosh(\Phi_B \alpha)d\alpha - \right.$$
$$\left. cosh(\Phi_B z)\int_z^1 c_A(\alpha)sinh(\Phi_B \alpha)d\alpha \right] \qquad 4.57$$

with $c_A(z)$ coming from eq. (4.54). Substitution of eq. (4.54) would permit factoring out two terms containing $c_A(0)$ times easily integrable functions of the hyperbolic trigonometric functions, but this course is not pursued here. The analytical solution for $c_B(z)$ can be written

$$c_B(z) = \frac{\cosh(\Phi_B z)}{\cosh(\Phi_B)} + \frac{\Phi_A^2 \Gamma_{AB}}{\Phi_B^2} \left[\sinh(\Phi_B z) \int_z^1 c_A(\alpha) \cosh(\Phi_B \alpha) d\alpha - \right.$$

$$\left. \cosh(\Phi_B z) \int_z^1 c_A(\alpha) \sinh(\Phi_B \alpha) d\alpha \right].$$

4.58

The solution for c_D is obtainable directly by two integrations and is given by

$$c_D(z) = 1 + \Gamma_{AD} \Phi_{2A}^2 \int_z^1 \int_0^\beta c_A^2(\alpha) d\alpha d\beta.$$

4.59

For this problem there is a single linear relationship between all four species which is

obtainable from taking the sum

$$D_A \frac{d^2 \hat{c}_A}{dx^2} + D_B \frac{d^2 \hat{c}_B}{dx^2} + D_C \frac{d^2 \hat{c}_C}{dx^2} + 2D_D \frac{d^2 \hat{c}_D}{dx^2} = 0$$

4.60

and performing two integrations per Chapter One to give

$$D_A(\hat{c}_A - \hat{c}_{As}) + D_B(\hat{c}_B - \hat{c}_{Bs}) + D_C(\hat{c}_C - \hat{c}_{Cs}) + 2D_D(\hat{c}_D - \hat{c}_{Ds}) = 0$$

4.61

which gives an expression for c_C through closure in terms of the solutions for c_A, c_B, and

c_D. So the entire problem's solution is given in terms of the Weierstrass Pe-function and

its integrals along with common elementary functions. The same basic situation applies

to Type III selectivity in general. If the first reaction is second-order or third-order, then

it can be solved analytically using the Weierstrass Pe-function procedures. If the second

reaction is first-order or zeroth-order, than a method such as variation of parameters can extend the analysis to solutions with integrals for the intermediate species. If the number of reactions in series is small, e.g. two, than relationships similar eq. (4.61) are available to help finish the analysis.

The general outlook for Type I selectivity and simultaneous reactions is good. These forms don't generally require any coupling between reactions, and independent second-order and/or third-order single reaction problems that occur as part of the set can be solved independently of the other reaction problems. If the problems are coupled, however, such as

$$
\begin{aligned}
A + B &\rightarrow P_1 \\
2A + B &\rightarrow P_2
\end{aligned}
\tag{4.62}
$$

or

$$
\begin{aligned}
A + B &\rightarrow P_1 \\
A + C &\rightarrow P_2,
\end{aligned}
\tag{4.63}
$$

then it can be shown in each case that there are "the number of coupled simultaneous reactions" fewer linear relationships between species than there are total species, i.e. no linear relationships between c_A and c_B in eq. (4.62) and only one between c_A, c_B and c_C in eq. (4.63). Consequently these problems cannot be reduced to a single ODE governing equation and are not amenable to the Weierstrass elliptic Pe-function treatment.

Eq. (4.38) is an example of Type II selectivity for parallel reactions of a single species. The concentration profile for the single reactant species can be easily derived using the Weierstrass elliptic Pe-function procedures in Chapters Two or Three. Developing analytical solutions for the product species, however, is only possible through direct integration of the solution for the reactant, and no closed forms are obtained just as was the case above for Type III selectivity and Van der Vusse kinetics. Roberts (1972) has presented results for a second-order reaction with either a first-order or a zeroth-order reaction in parallel, so this analysis proceeds no further. New results could be generated for third-order reactions in parallel with either a second-order, first-order, or zeroth-order reaction using the analytical solutions now available. Systems with three or four parallel reactions could also be examined. The kinetics in eq. (4.62) could be considered Type II or Type I, since it involves simultaneous reactions (Type I) as well as two species combining in parallel to form different products (Type II). Parallel reactions with more than one species do not appear amenable to treatment with the Weierstrass elliptic Pe-function methods described here.

In all of the above cases of multiple reactions it was assumed that the reactions were irreversible. If the reactions are allowed to be reversible, then the situation deteriorates nearly completely. The reason is simply that it is almost impossible to construct a set containing more than one elementary reversible reaction where a complete set of linear relationships exists between all of the species. For example,

$$3A \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} 3P, \quad r_{P_3} = k_{-3}\hat{c}_P^3 - k_3\hat{c}_A^3$$

$$2A \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2P, \quad r_{P_2} = k_{-2}\hat{c}_P^2 - k_2\hat{c}_A^2 \qquad 4.64$$

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} P, \quad r_{P_1} = k_{-1}\hat{c}_P - k_1\hat{c}_A$$

shows that it is not completely impossible to write such a system down, but it is severely restricted in possible form. The governing equations would take the form

$$D_A \frac{d^2\hat{c}_A}{dx^2} = -3r_{P_3} - 2r_{P_2} - r_{P_1} \qquad 4.65$$

$$D_P \frac{d^2\hat{c}_P}{dx^2} = 3r_{P_3} + 2r_{P_2} + r_{P_1} \qquad 4.66$$

and the importance of having stoichiometric coefficients that are equal in magnitude and opposite in sign is clearly noticeable.

The Weierstrass elliptic Pe-function procedures clearly have a place in the study of multiple reaction systems, but they generally fail to tell the whole story. No new equations for selectivity were developed that were free of integrals containing the Weierstrass Pe-function. So, although a step forward in the analyses of these problems has been made, there remains plenty of opportunity for further theoretical analysis.

Concluding Remarks

The transition to a solution of the Robin's problem is possible, but the present analysis retains awkward aspects. One formulation of the Robin's problem shows that

its solutions will behave similarly to the Dirichlet problem solutions of Chapters Two and Three. The effect of reaction order and Biot number on the single species irreversible reaction has been well documented now for orders up to three. The overall effectiveness factor decreases for increasing reaction orders at constant Biot number and generalized Thiele modulus. The physical significance of the Biot number in multiple species reactions has been called into question.

Increasing the reaction order of the kinetics above unity allows for more exotic elementary reactions such as those for autocatalysis. Surprising behavior leapt out after just a first quick look at the second-order case. The third-order case is virtually unexplored. The influence of negative values of the third-order modulus on the internal effectiveness factor is the highest priority problem at present. The analysis of the selectivity of reactions of different order or the Van der Vusse problem lead to equations with integrals of the concentration profile in terms of the Weierstrass elliptic Pe-function. These integrals have not yet yielded to analytical manipulation, but prospects are still bright. It is commonly acknowledged that it is easier to integrate a known function accurately than it is to approximately integrate the results of a finite difference solution of an ordinary differential equation.

The Weierstrass Pe-function solution methodology has an important, but more limited, role to play in the analysis of multiple reaction systems accompanied by diffusion. This chapter explored ways to apply the techniques from earlier chapters to such analyses. The Pe-function is most useful when a single-species ordinary differential equation can be derived for at least one species in the multiple reaction pathways. Some

other species' solutions involved integrals of the concentration profile in terms of the Weierstrass Pe-function. Some of these integrals may possess closed form solutions not discovered here.

This chapter hints at the breadth of application possible in simultaneous reaction and diffusion problems when one accepts the need for the Weierstrass elliptic Pe-function. The addition of 17 autocatalytic reactions to the Dirichlet boundary condition total from Chapters Two and Three combined with the tractability of the Robin's boundary condition problem and at least some of the series-parallel multiple reaction systems once again markedly increases the number of such reaction-diffusion problems that can be solved analytically.

CHAPTER 5
RECOMMENDATIONS AND FUTURE WORK

Recommendations

The work on second-order and third-order simultaneous conventional reaction and diffusion in a slab with the Dirichlet boundary condition has reached an advanced point. The identification of a species independent unifying governing equation has enabled significant new analyses to be made for the slab and laid the groundwork for similar analyses in other coordinate geometries. The parameter space size issue seems to be finally under control with the unifying governing equation format. New numerically useful dimensionless concentrations have been developed which possess good numerical properties. The internal effectiveness factor's behavior has been characterized quantitatively and semi-empirically in terms of a small number of characteristic moduli. Fine points of interpretation remain to be investigated for second-order kinetics, e.g. other regions of first-order behavior, effect of species multiplicity, effect of reverse reaction order, etc. These issues remain to be investigated for third-order kinetics as well. There are some additional outstanding questions about the shape of the third-order parameter space.

The unifying governing differential equation and boundary conditions plus the general expressions for the three moduli, containing the stoichiometric coefficients, given

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in Chapter Three present an opportunity to restructure the approach to teaching simultaneous reaction and diffusion in a slab. The rules for reducing the moduli for specific kinetic cases include the mandatory irreversible first-order reaction generally taught to graduate students in chemical engineering as a special case. Combining these with the $c''(z)$ dimensionless concentration offers future textbook authors a convenient setting to present comprehensive results for general small integer kinetics. The material, if properly presented, should certainly be within the reach of such students.

The Weierstrass elliptic Pe-function, and elliptic functions and integrals in general, are being omitted or minimized in many recent general advanced mathematical texts. Perhaps a representative sample of such texts was not available. Otherwise, this represents a disturbing trend. Most of the useful information obtained about the Weierstrass elliptic Pe-function came from sources over twenty years old. Yet the practical value of such functions is clearly demonstrated by this work. Furthermore, the Weierstrass elliptic Pe-function can be used to solve certain problems in chemical kinetics with two first-order ordinary differential equations. Perhaps it is time that some mention of this function be included in graduate level chemical engineering mathematics courses.

Future Work

While the developments described in this text have advanced the status of simultaneous reaction and diffusion research considerably, they do not tell the whole story. Many questions remain unanswered, and some probably remain unasked. The major areas needing work for the Dirichlet problem are for kinetics with a zeroth-order

reverse reaction and third-order autocatalysis. The developments for the Robin's problem could benefit from a more elegant treatment, especially for multiple species reactions.

As mentioned above, an analysis is still required for second-order and third-order problems with a zeroth-order reverse reaction. Most of the results shown in Chapters Two and Three will be valid for some such systems, at least in part. The analysis must develop criteria where these results are invalid, or in some sense violated physically, as well as developing methods to solve the governing equations in those cases. This requires identifying a condition under which the zeroth-order rate expression switches from its normal value, k_r, to its "extinguished" value. The "extinguished" value must also be identified. While this is zero for an irreversible zeroth-order reaction, it is likely to be something else in a reversible reaction, perhaps something like $k_f \hat{c}_A(x^*) \hat{c}_B(x^*)$.

Autocatalytic second-order reactions were found to possess unusual behavior. This was exemplified by the internal effectiveness factor results in the new quadrant of the parameter space made available when Φ_{1st}^2 can become negative. The behavior of third-order conventional reversible reactions spanned a broader range of internal effectiveness factor-generalized Thiele modulus behavior than second-order conventional reversible reactions. Third-order autocatalysis should present numerous opportunities for unusual behavior. First, second-order behavior is a special case of third-order behavior, and second, the third-order modulus, X, can become negative for autocatalytic reactions. Results for negative X have not been investigated to date.

There are a number of broad classes of kinetic rate forms in the context of second-order and third-order elementary reactions, e.g. second-order with second-order reversible, third-order with first-order reversible and so on. Within each broad class are various degrees of species multiplicity. It was seen for irreversible second-order and third-order reactions that species multiplicity reduced the dimension of the true parameter space required. This occurred in a straightforward manner. Species multiplicity in reversible reactions puts additional constraints on the physical data that go into the fundamental parameters, but no quantitative restrictions have been formulated. This area needs further analysis.

A major step forward in the theoretical analysis of simultaneous reaction and diffusion has been taken. The number of elementary reactions that can be studied through an analytical solution has increased tremendously from a mere handful to over fifty. Parameter space control has streamlined the new analyses over previous work in this field. The new solution method handles both the Dirichlet and Robin's problem at the surface. Analytical expressions for both the internal and overall effectiveness factors have been developed. There is also a role for the new solution method in the analysis of multiple reaction systems. Interesting reaction systems have not yet been analyzed including third-order autocatalytic reactions and reversible reactions with a zeroth-order component. Prospects for continued advances look good.

APPENDIX
NUMERICAL METHODS AND COMPUTER PROGRAMS

The graphical products presented in Chapters Two through Four would not have been possible without taking the theoretical solution of the simultaneous reaction and diffusion problems discussed there and completing their solution by satisfying the surface boundary condition. There were five significant practical considerations to be made.

(1)   Span the feasible parameter space from boundary to boundary.

(2)   Evaluate the Weierstrass elliptic Pe-function.

(3)   Solve an implicit equation for the dimensionless midplane concentration.

(4)   Generate one or more starting guesses for step (3).

(5)   Find the roots of the dimensionless reaction and diffusion equation.

The most significant problem with the parameter space boundary was its identification, discussed in Chapters Two through Four, after which developing a computer program to find the solution in that region was generally straightforward. There was one problem with boundaries not parallel to the parameter axes in the local graphics programs. This was never satisfactorily resolved and was dealt with manually.

The Weierstrass elliptic Pe-function, $\wp$, as used here, is an infinite series expansion in powers of z^2 and the two invariants, g_2 and g_3. Limiting z to a range from zero to unity by dimensionless scaling does not simplify this problem whatsoever. All such transformations effect the two invariants in a counterbalancing manner. Similarly,

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there were no transformations to the dimensionless concentration that changed the numerical values of the two invariants once the range of z was set from zero to one. Consequently, when the magnitudes of the invariants increase, more terms from the infinite series are required to evaluate $\wp$. The value of $\wp$ at the slab surface was generally less than ten and rarely as large as fifty over the range of parameters studied. This surprising result was due to cancellations between positive and negative terms in the series expansion. For unconverged midplane concentration guesses, however, $\wp$ sometimes became a very large number that was poorly calculated by the series expansion as coded in the program (up to the first 1000 terms). This problem was dealt with by improving initial guesses.

There was also a problem when the discriminant of the canonical polynomial was near zero. When the invariant magnitudes were also large, the infinite series for $\wp$ becomes one with large positive and negative terms with virtually equal magnitudes at the surface value of z. The limited precision of floating point numbers becomes a factor in totalling a sum of such differences. Careful testing revealed that in these cases one of the asymptotic limiting forms of the Weierstrass elliptic Pe-function, discussed in the text, was giving every bit as good a numerical value as the series expansion even before the numerical problem manifested. The subroutine for evaluating the Pe-function was coded to switch to one of these forms when necessary.

The nonlinear implicit equation for the dimensionless midplane concentration can be solved by any number of conventional methods. Two methods were used here. When the quality of initial guesses was less critical and $\wp$ was easily evaluated, the

secant method, see Borse (1985), was used to take advantage of its rapid convergence properties. In other cases the bisection method, see Borse (1985), was used, once the solution had been bracketed. Bisection was primarily employed to deal with larger invariant magnitudes, where a root of the reaction and diffusion equation could serve as one bound. The second bound was generally within 1% of this root in these cases. It was found by taking small steps toward the surface concentration.

The material in the Chapters Two and Three suggests many ways to estimate or bound the dimensionless midplane concentration, $c''(0)$. These methods were employed at different times to considerable advantage. The upper bound of one-half was useful for small invariant magnitudes in conventional reaction systems. The upper bound of the equilibrium root of the reaction and diffusion rate equation was useful at large invariant magnitudes. At intermediate invariant magnitudes combinations of the two bounds and estimators were employed to expedite convergence.

Finding the roots of the dimensionless reaction and diffusion concentration polynomials should be easy. There were no significant problems for second-order reactions, where the quadratic formula was used. There were significant problems for third-order reactions, where the analytical solution for cubic polynomials that relies on inverse trigonometric functions was used. Specifically, the numerical discrimination of the method when the argument of the inverse cosine function approached unity was poor. Errors as large as a factor of ten occurred in the desired root. It was necessary to test the roots in the cubic equation through back substitution, and if they were of low quality, than Newton's method was used to find revised root(s). Roots of high quality were

essential in bounding the solution from above at larger invariant magnitudes. The desired root was always the smallest, positive real root when using the c" formulation.

Thus a general strategy evolved. Choose a point in the feasible parameter space. Find the appropriate equilibrium root of the dimensionless rate expression. Assess the probability of having either large or small invariant magnitudes, and proceed with either the secant or bisection method generating additional initial guesses if necessary. Evaluate $\wp$ as required using a truncated series or an asymptotic form. Several hundred midplane concentration solutions, internal effectiveness factors, and generalized Thiele moduli values could be generated and printed to a file in two to three seconds real time on an 80486 based personal computer. In other words the solutions of the simultaneous reaction and diffusion problem in a slab could easily be incorporated into a fixed bed reactor simulation, for example, without deleterious effects on its performance.

Fortran codes for third-order reaction and diffusion problems are included here to document the research. The first code, GEN3RD, generates data for such third-order solution surfaces as Figures 3.7-3.9, where the second-order modulus, Ψ, is less than or equal to zero. Here the X-Φ_{1st} base is completely covered with feasible solutions. The second code, POSPSI3, shows modifications made to cope with a feasible parameter space boundary within the X-Φ_{1st} base plane, e.g. Figures 3.5 and 3.6. These codes are more sophisticated than the earlier codes for second-order systems which had not incorporated all the enhancements described above.

```
PROGRAM GEN3RD
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION PHI2(19),XSQRD(19),PLG(19),XLG(19)
```

```
C
        OPEN(UNIT=11,FILE='GEN3RD.OUT',STATUS='NEW')
        OPEN(UNIT=10,FILE='G3RD.INP',STATUS='OLD')
        OPEN(UNIT=12,FILE='GEN3RD.DAT',STATUS='NEW')
C
C    THE DESIRED VALUE OF PSI IS ENTERED IN G3RD.INP
C
C    THIS PROGRAM CALCULATES THE MIDPLANE CONCENTRATION AND
C    INTERNAL EFFECTIVENESS FACTOR, PLUS GENERAL THIELE
C    MODULUS AND THE FOLLOWING WEIGHTED VALUE,
C    DISCRIMINANT(DELTA(G2,G3))/ABS(PARTS OF DELTA), FOR
C    THE GENERAL THIRD-ORDER REACTION AND DIFFUSION PROBLEM
C    IN A SLAB IN THE THREE PARAMETER FORMULATION:
C    X, PSI, PHI(FIRST)**2 USING THE WEIERSTRASS
C    ELLIPTIC PE FUNCTION OR ONE OF ITS ASYMPTOTIC FORMS.
C
C *** THE PROGRAM IS FOR A FIXED NONPOSITIVE PSI,
C
C    AND A RANGE OF X THAT EXTENDS THE INTERNAL
C    EFFECTIVENESS FACTORS DOWN TO ABOUT 0.1 OR SLIGHTLY LESS
C    THE PROGRAM PRESUMES THE DIMENSIONLESS CONCENTRATION,
C    C", IS USED IN DEVELOPING THE GOVERNING EQUATIONS
C
C    FMDPLA HOLDS THE CONCENTRATION FUNCTION'S MIDPLANE VALUE
C    CEQ HOLDS THE EQUIL. CONCENTRATION (SMALLEST,POSITIVE)
C    C() IN THE PROGRAM ARE PE-FUNCTION COEFFICIENTS
C    PHIG IS THE GENERALIZED THIELE MODULUS
C    PHI2 IS PHI(FIRST)**2, SI IS PSI, AND X2 IS X
C    ETA IS THE INTERNAL EFFECTIVENESS FACTOR
C    PLG,XLG,ET ARE LOG SCALED VALUES OF PHI,X2 AND ETA
C
        READ(10,*)SI
        IF(SI.LT.1.E-5)THEN
         XN1=DLOG10(0.01)
         DEL=4./18.
        ELSE
         XN1=DSQRT(3.*PSI)
         DEL=(2.-DLOG10(XN1))/18.
        END IF
C
C    CREATE A 19 BY 19 GRID OF MIDPLANE SOLUTIONS, ETC.
C    WITH REGULAR SPACING ON LOGARITHMIC AXES
C
        DO 15 I=1,19
         EXPON=XN1+(I-1)*DEL
         PLG(I)=(I-1)*DEL
         PHI2(I)=10.**EXPON
15      CONTINUE
        XN2=DLOG10(3.375E-6)
        DEL=2./3.
        DO 16 I=1,19
```

```
          EXPON=XN2+(I-1)*DEL
          XSQRD(I)=10.**EXPON
          XLG(I)=(I-1)*DEL
16     CONTINUE
C
C  DO I FOR THE X2'S DESIRED
C
       WRITE(11,899)SI
899    FORMAT(1X,'GENERAL THIRD-ORDER SOLUTIONS FOR PSI=',
     $ E15.7/1X,5X,'PHI2',8X,'XSQRD',9X,'FMDPLA',6X,
     $ 'ETA',9X,'DEL/ABS',7X,'PHIGEN')
       DO 100 I=1,19
        X2=XSQRD(I)
C
C  DO J FOR THE NUMBER OF PHI(FIRST)**2'S DESIRED
C  (SMALLEST TO LARGEST)
C
        DO 200 J=1,19
         P2=PHI2(J)
C
C FIND ROOTS OF THE DIMENSIONLESS REACTION AND DIFFUSION
C EQUATION IN SUBROUTINE ROOT
C
         CALL ROOT(P2,SI,X2,CEQ)
C
C  FIND THE DIMENSIONLESS MIDPLANE CONCENTRATION SOLUTION TO
C  THE BOUNDARY CONDTITIONS IN SUBROUTINE SOLV2
C
         CALL SOLV2(P2,SI,X2,FMDPLA,DELTA,CEQ)
         F0=FMDPLA
         ETA=DSQRT(((((-X2*F0/2.+2.*SI/3.)*F0-P2)*F0+2.)*F0)
         F1=CEQ
         PHIG=1./DSQRT(((((-X2*F1/2.+2.*SI/3.)*F1-P2)*
     $     F1+2.)*F1)
         WRITE(11,900)P2,X2,F0,ETA,DELTA,PHIG
         ET=DLOG10(ETA)+1.0000
C
C  PREPARE A LOGARITHMICALLY SCALED OUTPUT FILE FOR INPUT
C  TO GRAPHICAL PLOTTING PROGRAMS
C
         WRITE(12,902)PLG(J),XLG(I),ET
200     CONTINUE
100     CONTINUE
900     FORMAT(1X,F10.5,1X,E15.7,1X,F10.7,1X,F10.7,
     $ 2X,E15.7,1X, F10.5)
902     FORMAT(3(F10.6,1X))
       STOP
       END

       SUBROUTINE SOLV2(P2,SI,X2,FMDPLA,DELTA,CEQ)
       IMPLICIT REAL*8 (A-H,O-Z)
```

```
C
C     APPLY THE SECANT METHOD OR THE BISECTION METHOD TO
C     CALCULATE C"(0) FROM THE ANALYTICAL SOLUTION WITH THE
C     WEIERSTRASS PE FUNCTION
C
C     P2 IS (PHI)FIRST**2
C     P2n ARE POWERS OF P2
C     SI IS PSI
C     X2 IS X
C     G2n ARE COEFFICIENTS OF C"(0) IN INVARIANT GE2
C     G3n ARE COEFFICIENTS OF C"(0) IN INVARIANT GE3
C     Sn  ARE COEFFICIENTS IN C"(Z) (NUMERATOR AND DENOMINATOR)
C     DCn ARE COEFFICIENTS IN DC"/DZ EXPRESSION
C     FMDPLA IS C"(0), COMES FROM C0 AND C1 AND CNEW
C     DELTA IS -(G2**3-27*G3**2)/(ABS(G2**3)+27*G3**2)
C
      P22=P2*P2
      P23=P22*P2
      G21=-X2*X2/4.
      G22=X2*SI/3.
      G23=-X2*P2/2.
      G24=X2
      G25=P22/12.-SI/3.
C G31-G34 SHARE A FACTOR WITH G21-G24, EXPLOIT THIS
      G314=(X2*P2/6.-SI*SI/18.)/X2
      G35=SI*P2/36.-P23/216.-X2/8.
      S1=6.*X2
      S2=-6.*SI
      S3=6.*P2
      S4=-6.
      S5=-3.*X2
      S6=2.*SI
      S7=-P2
C
C CHOOSE SMALLEST OF 0.5, CEQ FOR FIRST GUESS FOR FMDPLA
C
      C0=0.50
      IF(C0.GE.CEQ)THEN
       C0=CEQ
      END IF
C
C CHOOSE SECOND GUESS FOR FMDPLA
C
      C1=.99*C0
C
      GE2=(((G21*C0+G22)*C0+G23)*C0+G24)*C0
C
C   THIS WAS JUST THE PART OF GE2 COMMON TO BOTH INVARIANTS
C
      GE3=G314*GE2 + G35
      GE2=GE2+G25
```

```
C
C USE SECANT METHOD FOR DIFFUSION FREE REGIONS,
C AND USE THE BISECTION METHOD FOR
C DIFFUSION LIMITED REGIONS
C
      IF(C0.GT.0.30)THEN
C
C PROCEED WITH SECANT METHOD
C
C   SUBROUTINE WEIER EVALUATES THE PE FUNCTION AND DELTA
C
      CALL WEIER(GE2,GE3,PE,DELTA)
      F0=C0+(((S1*C0+S2)*C0+S3)*C0+S4)/
     $ (12.*PE+(S5*C0+S6)*C0+S7)
      SAFE=0.
10    CONTINUE
       SAFE=SAFE+1.
        IF(SAFE.GT.50.)THEN
         WRITE(11,*)'SAFE=51',C0,F0,C1,F1
         STOP
        END IF
       GE2=(((G21*C1+G22)*C1+G23)*C1+G24)*C1
       GE3=G314*GE2 + G35
       GE2=GE2+G25
       CALL WEIER(GE2,GE3,PE,DELTA)
       F1=C1+(((S1*C1+S2)*C1+S3)*C1+S4)/
     $ (12.*PE+(S5*C1+S6)*C1+S7)
       IF((F1-F0).EQ.0.000)THEN
        WRITE(11,*)'P2=',P2,' X2=',X2,'  F1-F0=0'
        STOP
       END IF
       CNEW=(C0*F1-C1*F0)/(F1-F0)
       C0=C1
       F0=F1
       TEST=ABS((CNEW-C1)/C1)
       C1=CNEW
      IF(TEST.GT.0.000001)GO TO 10
      FMDPLA=C1
C
C BISECTION LOGIC FOR (LARGE?) INVARIANTS
C
      ELSE
C
C GUESS PE IS LARGE AT A BAD GUESS, I.E.
C SUM(SI*C0)/(12.PE-OTHER SI)
C GIVES 0.=C0+1/INFINITY=C0 TO KEEP ITERATION PROCEEDING
C
        F0=C0
        CALL WEIER(GE2,GE3,PE,DELTA)
         IF(PE.GT.1.E30)THEN
           F0=C0
```

```
          ELSE
            F0=C0+(((S1*C0+S2)*C0+S3)*C0+S4)/
     $      (12.*PE+(S5*C0+S6)*C0+S7)
          END IF
          STEP=.01*C0
C
          COUNT=1.
          C1=C0
          F1=F0
200       CONTINUE
            F0=F1
            COUNT=COUNT+1.
C
C DECREMENT C1 TO FIND RANGE FOR BISECTION TO OPERATE IN
C
          C1=C1-STEP
          GE2=(((G21*C1+G22)*C1+G23)*C1+G24)*C1
          GE3=G314*GE2 + G35
          GE2=GE2+G25
          CALL WEIER(GE2,GE3,PE,DELTA)
          IF(PE.GT.1.E30)THEN
            F1=C1
          ELSE
            F1=C1+(((S1*C1+S2)*C1+S3)*C1+S4)/
     $      (12.*PE+(S5*C1+S6)*C1+S7)
          END IF
          IF(F1*F0.GT.0.00.AND.COUNT.LT.100.)GO TO 200
          IF(COUNT.GE.100.)THEN
            WRITE(11,*)'COUNT EXCEEDED IN BRACKETING,
     $      PHIFIRST**2=',P2
            STOP
          END IF
C
          IF(C1.LT.0.00)THEN
            WRITE(11,*)'P2=',P2,' X2=',X2,' BISECTION
     $ RANGE INTO NEGATIVE'
            STOP
          END IF
          CLOWER=C1
          CUPPER=C1+STEP
          FUPPER=F0
          FLOWER=F1
          COUNT=1
201       CONTINUE
            COUNT=COUNT+1.
            C1=(CUPPER+CLOWER)/2.
            GE2=(((G21*C1+G22)*C1+G23)*C1+G24)*C1
            GE3=G314*GE2 + G35
            GE2=GE2+G25
            CALL WEIER(GE2,GE3,PE,DELTA)
            IF(PE.GT.1.E30)THEN
```

```fortran
          F1=C1
        ELSE
          F1=C1+(((S1*C1+S2)*C1+S3)*C1+S4)/
     $      (12.*PE+(S5*C1+S6)*C1+S7)
        END IF
        IF(F1*FUPPER.LT.0.00)THEN
          CLOWER=C1
        ELSE
          CUPPER=C1
          FUPPER=F1
        END IF
        IF(COUNT.GT.200)THEN
          WRITE(11,*)'BISECTION BOGGING DOWN'
          WRITE(11,*)'CU,CL,C1=',CUPPER,CLOWER,C1
          WRITE(11,*)'FU,F0,F1=',FUPPER,F0,F1
          STOP
        END IF
C
C SPECIAL LOGIC FOR LACK OF SIGNIFICANT FIGURES
C
        C0TEST=ABS(CUPPER-CLOWER)/CUPPER
        IF(C0TEST.LT.1.E-10)THEN
          F1=0.
        END IF
C
        IF(ABS(F1).GT.1.E-08)GO TO 201
        FMDPLA=C1
C
C END OVERALL IF/ELSE/END IF ON C0 VS. 0.30
C
      END IF
C
      RETURN
      END
C
C
      SUBROUTINE WEIER(G2,G3,PE,DELTA)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION C(1000)
C
C  THIS SUBROUTINE IS A REVISION OF A MORE GENERAL
C  SUBROUTINE, AND IT CALCULATES THE WEIERSTRASS PE-
C  FUNCTION STRICTLY AT THE SURFACE POSITION, Z = 1
C
C TEST THE INVARIANTS OF THE CURRENT GUESS
C
      DELTA=-(G2/27.-(G3/G2)**2)/(ABS(G2/27.)+(G3/G2)**2)
      IF(ABS(DELTA).LT.1.E-3.AND.G2.GT.0.00)THEN
C
C USE A LIMITING FORM FOR PE(1) IN THIS CASE
C
```

```fortran
      R=DSQRT(G2/12.)
      X3R=3.*R
      IF(G3.LT.0.00)THEN
       DENOM=(SINH(DSQRT(X3R)))**2
       IF(DENOM.NE.0.00)THEN
        PE= R + X3R/DENOM
       ELSE
        STOP
       END IF
      ELSE
       DENOM=(SIN(DSQRT(X3R)))**2
       IF(DENOM.NE.0.00)THEN
        PE= -R + X3R/DENOM
       ELSE
        STOP
       END IF
      END IF
C
      ELSE
C
C  COMPUTE THE COEFFICIENTS OF PE FROM K=2 UP BASED ON G2,G3

C  AND EVALUATE PE(1;G2,G3)
C
      C(2)=G2/20.
      C(3)=G3/28.
      C(4)=C(2)*C(2)/3.
      C(5)=3.*C(2)*C(3)/11.
      C(6)=(2.*(C(2)**3)+3.*C(3)*C(3))/39.
      C(7)=2.*C(2)*C(2)*C(3)/33.
      PE=1.
      DO 10 I=2,7
       PE=PE+C(I)
10    CONTINUE
       K=7
C
C  CODE WAS MODIFIED TO RUN ON A PC INSTEAD OF DEC VAX
C  WHICH NECESSITATED DROPPING DO WHILE STRUCTURES FOR
C  THE AVAILABLE VERSION OF DOS FORTRAN
C
C        DO WHILE(ABS(C(K)).GT.1.E-12)
20    CONTINUE
      K=K+1
      MSTOP=K-2
      SUM=0.
       DO 30 M=2,MSTOP
        SUM=SUM+C(M)*C(K-M)
30     CONTINUE
      C(K)=3.*SUM/((2.*K+1.)*(K-3.))
      PE=PE+C(K)
      IF(C(K).GT.0.00)THEN
```

```
          TEST=ABS(C(K)/PE)
         ELSE
          TEST=1.E-5
         END IF
         IF(PE.GT.1.0D+50)THEN
          TEST=0.
         END IF
          IF(K.GT.999)THEN
           WRITE(11,101)G2,G3,PE,C(K)
101        FORMAT(1X,'RAN OUT OF COEFFS AT G=',2E15.8/1X,
     $   'PE,C(1000)=', 2E15.8)
           TEST=0.
          END IF
         IF(TEST.GT.1.E-10)GO TO 20
C     END DO
C
      END IF
C
      RETURN
      END
C
      SUBROUTINE ROOT(PHI1ST,SI,XSQRD,CEQ)
      IMPLICIT REAL*8 (A-H,O-Z)
C
C THIS SUBROUTINE CALCULATES THE SMALLEST POSITIVE ROOT OF
C THE GENERAL CUBIC RATE EXPRESSION(PHI(FIRST)**2,PSI,XSQRD)
C TO BE USED TO CALCULATE THE GENERALIZED MODULUS, OR AS A
C STARTING GUESS FOR THE SOLV2 ITERATION.  THE TRIGONOMETRIC
C METHOD, SEE CRC MATH HANDBOOK OR PERRY'S HANDBOOK, IS USED
C FOR MOST ROOTS.
C
      PI=3.141592654
      P2=PHI1ST
      SI2=SI*SI
      SI3=SI*SI2
      X=XSQRD
      XX=X*X
      XXX=X*XX
      A=(3.*X*P2-SI2)/(3.*XX)
      B=(9.*SI*P2*X-27.*XX-2.*SI3)/(27.*XXX)
      ROOTST=1./(2.*X)**2 + (P2/(3.*X))**3 -
     $ (SI/XX)*(P2/(6.*X))
     $ +(1./X)*(SI/(3.*X))**3 - (P2*P2/3.)*(SI/(6.*XX))**2
C
C BRANCH FOR THREE REAL ROOTS OR ONE REAL ROOT
C
      IF(ROOTST.GT.0.00)THEN
C
C THIS LOGIC FOR ONE REAL ROOT:
C
         ONETST=-B/2.+DSQRT(ROOTST)
```

```fortran
         IF(ONETST.LT.0.00)THEN
           CAPA=-(-ONETST)**0.333333333
         ELSE
           CAPA=(ONETST)**0.333333333
         END IF
         TWOTST=-B/2.-DSQRT(ROOTST)
         IF(TWOTST.LT.0.00)THEN
           CAPB=-(-TWOTST)**0.333333333
         ELSE
           CAPB=(TWOTST)**0.333333333
         END IF
         Y1=CAPA+CAPB
         CEQ=Y1+SI/(3.*X)
C
         ELSE
C
C THIS LOGIC FOR THREE REAL ROOTS:
C
         ANGARG=DSQRT(-27.*(B/A)*(B/A)/(4.*A))
C
C THIS LOGIC COVERS CASES WHERE ANGARG WAS PROBABLY ONE BUT
C WAS NOT LESS THAN OR EQUAL TO ONE BECAUSE OF A SMALL
C ROUND-OFF IN THE DIFFERENCE OF TWO VERY LARGE NUMBERS
C
         IF(ANGARG.GT.1.0000000000)THEN
           RNDOFF=1.E-10
           IF(ANGARG-RNDOFF.LT.1.00000)THEN
             ANGARG=1.
           ELSE
             WRITE(11,905)SI,X,ANGARG
             STOP
           END IF
         END IF
905      FORMAT(1X,2E15.7, 'ACOS ARGUMENT=',E15.7)
         ANG=ACOS(ANGARG)
         PREMUL=2.*DSQRT(-A/3.)
         IF(B.GE.0.00)THEN
           Y1=-PREMUL*COS(ANG/3.)
           Y2=-PREMUL*COS((ANG+2.*PI)/3.)
           Y3=-PREMUL*COS((ANG+4.*PI)/3.)
         ELSE
           Y1=PREMUL*COS(ANG/3.)
           Y2=PREMUL*COS((ANG+2.*PI)/3.)
           Y3=PREMUL*COS((ANG+4.*PI)/3.)
         END IF
         ADDER=SI/(3.*X)
         CEQ1=Y1+ADDER
         CEQ2=Y2+ADDER
         CEQ3=Y3+ADDER
C
C SORT FOR THE SMALLEST POSITIVE ROOT WHEN THERE ARE THREE.
```

```
C FIRST ORDER THE ROOTS, CEQA IS SMALLEST
C
        IF(CEQ1.LT.CEQ2)THEN
          CEQA=CEQ1
          CEQB=CEQ2
        ELSE
          CEQA=CEQ2
          CEQB=CEQ1
        END IF
C
        IF(CEQ3.LE.CEQA)THEN
          CEQC=CEQB
          CEQB=CEQA
          CEQA=CEQ3
        ELSE
          IF(CEQ3.GE.CEQB)THEN
            CEQC=CEQ3
          ELSE
            CEQC=CEQB
            CECB=CEQ3
          END IF
        END IF
C
        IF(CEQC.LT.0.0000)THEN
          WRITE(11,800)P2,SI,X
800     FORMAT(1X,'PHIFIRST=',F10.6,' PSI=',E15.7,' XSQRD=',
     $ E15.7/1X,'ALL CEQ ARE LESS THAN ZERO')
          STOP
        END IF
C
C PICK THE SMALLEST POSITIVE ROOT
C
        IF(CEQB.GT.0.00)THEN
          IF(CEQA.GT.0.00)THEN
            CEQ=CEQA
          ELSE
            CEQ=CEQB
          END IF
        ELSE
          CEQ=CEQC
        END IF
C
C
CC
        END IF
C
C CHECK ACCURACY OF ROOT CALCULATION AGAINST ORIGINAL
C POLYNOMIAL
C
        TEST=ABS(((X*CEQ-SI)*CEQ+P2)*CEQ)-1.
        IF(TEST.GT.1.E-7)THEN
```

```
C
C THIS LOGIC WAS ESSENTIAL AND NOT PRECAUTIONARY.  THE
C INVERSE TRIG FUNCTION NEAR UNITY WAS NOT SUFFICIENTLY
C PRECISE.  ROOTS OF THE EQUATION WERE OFF BY MORE THAN
C A FACTOR OF TEN IN THE PARAMETER DOMAIN STUDIED IN
C CHAPTER 3 AT TIMES.  IN THAT CASE
C
C TRY AGAIN (WITH NEWTON'S METHOD) TO FIND CEQ
C
      DF1=3.*X
      DF2=2.*SI
      C0=0.
205   CONTINUE
       F=((X*C0-SI)*C0+P2)*C0-1.
       DF=(DF1*C0-DF2)*C0+P2
       IF(DF.EQ.0.00.AND.ABS(F).GT.1.E-8)THEN
        C1=(1.+1.E-10)*C0
       ELSE
        C1=C0-F/DF
       END IF
       C0=C1
      IF(ABS(F).GT.1.E-8)GO TO 205
C
      BA=X
      BB=X*C1-SI
      BC=(X*C1-SI)*C1+P2
      ARG=BB*BB-4.*BA*BC
      IF(ARG.GE.0.000)THEN
       CEQ1=C1
       CEQ2=(-BB+DSQRT(ARG))/(2.*BA)
       CEQ3=(-BB-DSQRT(ARG))/(2.*BA)
C
C SORT FOR THE SMALLEST POSITIVE ROOT WHEN THERE ARE THREE
C FIRST ORDER THE ROOTS, CEQA IS SMALLEST
C
       IF(CEQ1.LT.CEQ2)THEN
        CEQA=CEQ1
        CEQB=CEQ2
       ELSE
        CEQA=CEQ2
        CEQB=CEQ1
       END IF
C
       IF(CEQ3.LE.CEQA)THEN
        CEQC=CEQB
        CEQB=CEQA
        CEQA=CEQ3
       ELSE
        IF(CEQ3.GE.CEQB)THEN
         CEQC=CEQ3
        ELSE
```

```
          CEQC=CEQB
          CECB=CEQ3
        END IF
      END IF
C
      IF(CEQC.LT.0.0000)THEN
        WRITE(11,800)P2,SI,X
        STOP
      END IF
C
C PICK THE SMALLEST POSITIVE ROOT
C
        IF(CEQB.GT.0.00)THEN
          IF(CEQA.GT.0.00)THEN
            CEQ=CEQA
          ELSE
            CEQ=CEQB
          END IF
        ELSE
          CEQ=CEQC
        END IF
C
        ELSE
          CEQ=C1
        END IF
      END IF
      RETURN
      END
```

This is the end of the Fortran code for the nonpositive Ψ cases of third-order simultaneous reaction and diffusion in a slab. Only the revised main portion of the program code will be given for the case of positive Ψ values, since the subroutines were not altered.

```
      PROGRAM POSPSI3
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION PHI2(19),XSQRD(19),PLG(19),XLG(19)
C
C THIS IS A REVISION TO GEN3RD. FOR TO EXCLUDE A REGION OF
C PARAMETER SPACE FOR X LESS THAN THE 3 REAL ROOT LOWER
C BOUNDARY SURFACE FOR MULTIPLE ROOTS, CHAPTER 3
C
      OPEN(UNIT=11,FILE='GEN3RD.OUT',STATUS='NEW')
      OPEN(UNIT=10,FILE='G3RD.INP',STATUS='OLD')
      OPEN(UNIT=12,FILE='GEN3RD.DAT',STATUS='NEW')
```

```
C
C    THIS PROGRAM CALCULATES THE MIDPLANE CONCENTRATION AND
C    INTERNAL EFFECTIVENESS FACTOR, PLUS GENERALIZED THIELE
C    MODULUS AND THE WEIGHTED DELTA(G2,G3)/ABS(PARTS OF
C    DELTA), FOR THE GENERAL THIRD-ORDER REACTION AND
C    DIFFUSION PROBLEM IN A SLAB IN THE THREE PARAMETER
C    FORMULATION:   X, PSI, PHI(FIRST)**2 USING THE
C    WEIERSTRASS ELLIPTIC PE FUNCTION OR ONE OF ITS ASYMPTOTIC
C    FORMS.
C      THE PROGRAM IS FOR FIXED PSI, PHI(FIRST)**2 GREATER
C      THAN ONE- THIRD OF ROOT PSI, WHEN PSI IS POSITIVE, AND
C      A RANGE OF X THAT EXTENDS THRU INTERNAL
C      EFFECTIVENESS FACTORS OF ABOUT 0.1
C
C    FMDPLA HOLDS THE CONCENTRATION FUNCTION'S MIDPLANE VALUE
C    CEQ HOLDS THE EQUIL. CONCENTRATION (SMALLEST,POSITIVE)
C    C() IN THE PROGRAM ARE PE-FUNCTION COEFFICIENTS
C    PHIG IS THE GENERALIZED THIELE MODULUS
C    PHI2 IS PHI(FIRST)**2, SI IS PSI, AND X2 IS X
C    ETA IS THE INTERNAL EFFECTIVENESS FACTOR
C    PLG,XLG,ET ARE LOG SCALED VALUES OF PHI,X2 AND ETA
C
      READ(10,*)SI
      IF(SI.LT.1.E-5)THEN
       XN1=DLOG10(0.01)
       DEL=4./18.
      ELSE
       XN1=DLOG10(DSQRT(3.*SI))
       DEL=(2.-XN1)/18.
      END IF
      DO 15 I=1,19
       EXPON=XN1+(I-1)*DEL
       PLG(I)=(I-1)*DEL
       PHI2(I)=10.**EXPON
15    CONTINUE
      XN2=DLOG10(3.375E-6)
      DEL=2./3.
      DO 16 I=1,19
       EXPON=XN2+(I-1)*DEL
       XSQRD(I)=10.**EXPON
       XLG(I)=(I-1)*DEL
16    CONTINUE
C
C  DO I FOR THE PHI(FIRST)**2'S DESIRED
C
      WRITE(11,899)SI
899   FORMAT(1X,'GENERAL THIRD-ORDER SOLUTIONS FOR PSI=',
     $ E15.7/1X, 5X,'PHI2',8X,'XSQRD',9X,'FMDPLA',
     $ 6X,'ETA',9X,'DEL/ABS',7X,'PHIGEN')
      DO 100 II=1,19
       I=20-II
```

```
        P2=PHI2(I)
        CODE=1.
        IF(I.NE.1)THEN
        X2STAR=(9.*P2*SI-2.*P2*P2*P2-2.*
     $  DSQRT((P2*P2-3.*SI)**3))/27.
        ELSE
C
C IF I=1, THEN P2**2-3SI = 0, BUT IF ROUND-OFF IS NEGATIVE,
C DSQRT FUNCTION WILL FAIL
C
        X2STAR=(9.*P2*SI-2.*P2*P2*P2)/27.
        END IF
C
C DO J FOR THE NUMBER OF X2'S DESIRED (LARGEST TO
C SMALLEST SINCE LARGEST IS A CONSTANT)
C
        DO 200 JJ=1,19
         J=20-JJ
         X2=XSQRD(J)
C
C SPECIAL PARAMETER REGION AVOIDANCE LOGIC ON X2
C
         IF(X2.LE.X2STAR)THEN
C
          IF(CODE.GT.0.00)THEN
           XUSE=1.0000001*X2STAR
           CALL ROOT(P2,SI,XUSE,CEQ)
           CALL SOLV2(P2,SI,XUSE,FMDPLA,DELTA,CEQ)
           F0=FMDPLA
           ETA=DSQRT((((-XUSE*F0/2.+2.*SI/3.)
     $     *F0-P2)*F0+2.)*F0)
           F1=CEQ
           PHIG=1./DSQRT((((-XUSE*F1/2.+2.*SI/3.)
     $     *F1-P2)*F1+2.)*F1)
           WRITE(11,910)P2,X2,F0,ETA,DELTA,PHIG
           ET=DLOG10(ETA)+1.0000
           WRITE(12,902)PLG(I),XLG(J),ET
           CODE=-1.
          ELSE
C
C DON'T RECALCULATE AFTER X2 DROPS BELOW X2STAR
C
           WRITE(12,902)PLG(I),XLG(J),ET
          END IF
C
         ELSE
C
          CALL ROOT(P2,SI,X2,CEQ)
          CALL SOLV2(P2,SI,X2,FMDPLA,DELTA,CEQ)
          F0=FMDPLA
          ETA=DSQRT((((-X2*F0/2.+2.*SI/3.)*F0-P2)*F0+2.)*F0)
```

```
        F1=CEQ
        PHIG=1./DSQRT(((((-X2*F1/2.+2.*SI/3.)
     $    *F1-P2)*F1+2.)*F1)
        WRITE(11,900)P2,X2,F0,ETA,DELTA,PHIG
        ET=DLOG10(ETA)+1.0000
        WRITE(12,902)PLG(I),XLG(J),ET
C
        END IF
C
200     CONTINUE
100   CONTINUE
900   FORMAT(1X,F10.5,1X,E15.7,1X,F10.7,1X,
     $ F10.7,2X,E15.7,1X,F10.5)
902   FORMAT(3(F10.6,1X))
910   FORMAT(1X,F10.5,1X,E15.7,'*',1X,F10.7,1X,
     $ F10.7,1X,E15.7,1X,F10.5)
      STOP
      END
```

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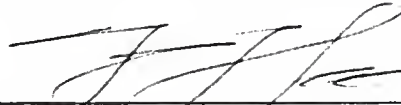Ince, E.L., 1927, <u>Ordinary Differential Equations</u>, Longman, Green, & Co., ltd., London.

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BIOGRAPHICAL SKETCH

David Koopman was born in Plymouth, Wisconsin, on July 8, 1954. He attended public schools in that state, graduating fifth in his high school class in 1972. David attended the University of Wisconsin, Marshfield, Wood Co. campus for two years where he earned an associate degree. In the fall of 1974, David was accepted for admission in the Department of Chemical Engineering, College of Engineering, University of Wisconsin in Madison. There he earned a BS degree in chemical engineering in 1976. David worked in industry for nine years, five with Ethyl Corp. in Baton Rouge, LA, and four with Rubicon, Inc. in Geismar, LA. Before starting his graduate work at the University of Florida, David completed several continuing education courses relevant to the field of chemical engineering as well as earning 25 credits at Louisiana State University in Baton Rouge. The University of Florida's Graduate Council awarded David a fellowship to start his graduate program. While at UF, David also was the recipient of the Tennessee Eastman Kodak fellowship given to outstanding students in the Chemical Engineering department. David was awarded an MS degree in chemical engineering in the summer of 1987 by the University of Florida and received his PhD in chemical engineering in the fall of 1992 with a perfect 4.0 grade point average.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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Professor of Chemical Engineering

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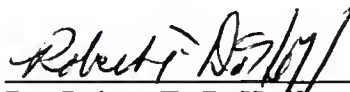
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This dissertation was submitted to the Graduate Faculty of the College of Engineering and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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